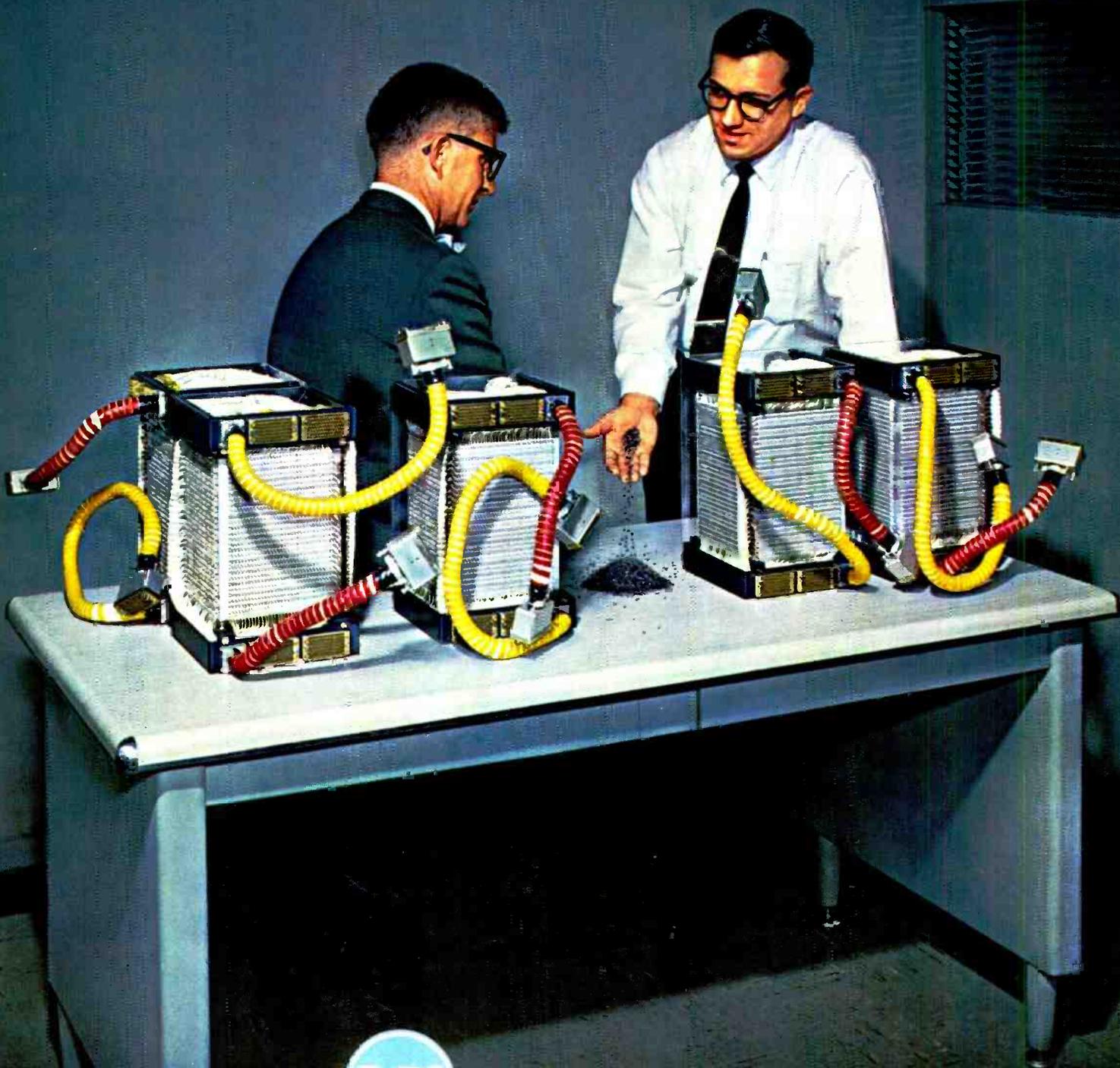


RCA ENGINEER



Vol. 5—No. 4 • December, 1959—January, 1960

OBJECTIVES

To disseminate to RCA engineers technical information of professional value.

To publish in an appropriate manner important technical developments at RCA, and the role of the engineer.

To serve as a medium of interchange of technical information between various engineering groups at RCA.

To create a community of engineering interest within the company by stressing the interrelated nature of all technical contributions.

To help publicize engineering achievements in a manner that will promote the interests and reputation of RCA in the engineering field.

To provide a convenient means by which the RCA engineer may review his professional work before associates and engineering management.

To announce outstanding and unusual achievements of RCA engineers in a manner most likely to enhance their prestige and professional status.



OUR COVER

Magnetic memory stacks for the RCA-501 computer—the "materials" in this case are the ferrite cores spilling over from the hand of Joseph J. Sacca, Manager of Magnetic Materials Development, who has played a prominent role in their development at the Needham Materials Operation, Semiconductor and Materials Division, Needham Heights, Mass. The whole assembly—from cores to wired-up stack—is fabricated at Needham prior to shipment to IEP in Camden for installation in the 501. Lloyd B. Smith, Manager of Production Methods and Process Development during initial manufacture of the stacks (he is now Manager of Engineering Services at Needham), was the man behind the techniques of production. (On page 16, Mr. Sacca tells about the "Development of Square-Loop Ferrite Memory Cores.")

MATERIALS FOR GROWTH

Growth is an attribute of healthy mankind. We grow in size and number, as do other living things. More significantly, we grow in knowledge and understanding, and in our ability to appreciate and utilize information. Man is increasingly demanding information that is more acceptable in form, quality, and cost—when and where he wants it.

Electronics provides the fastest and most versatile means for supplying information. The highest speed of propagation has already been attained by using the fleetest elementary particles, particularly electrons and photons, to carry messages. Versatility, however, continues to increase. The increase is provided in large measure by the growing number and uses of materials—the different communities of atoms with their different properties.

It is impressive that just three elementary particles, the electron, proton, and neutron, can form over a hundred different atoms. These can combine to provide millions of compounds, and the compounds can unite to form countless materials. There is practical allure in the potentialities of an infinite number of materials and properties. Research in this field should always be interesting, because the possibility of finding new and greatly intensified electronic and other effects is ever present.

In recent years, there has been a great upswing in research on electronically active solids, notably semiconductors, photoconductors, photovoltaics, electron emitters, phosphors, and magnetics (ferrites). Those materials have already been incorporated in devices that provide useful means for detecting, converting, processing, storing, transmitting, and reproducing information. In the future, existing devices will be improved by the advent of superior new materials, and other useful devices should come from research on materials such as ferroelectrics, electrets, superconductors, and thermoelectrics.

We are experiencing a remarkable increase in our ability to utilize obscure and small-scale effects in special materials. The short-range quantum-mechanical tunnel effect of electrons has recently been put to use in the tunnel diode. Electrons that exhibit negative effective masses in certain materials show promise of being useful in future devices. Bound electrons have been made to function as amplifier agents in masers and parametric amplifiers. A next step is to utilize nuclear particles, as we have set out to do in studies of nuclear magnetic resonance, in research using the five-megawatt nuclear-fission reactor of Industrial Reactor Laboratories, and in our contribution to Project Matterhorn, whose goal is the production of useful energy from thermonuclear fusion.

Our increasing ability to utilize small-scale phenomena becomes especially valuable in our program to decrease the size and cost of electronic apparatus, while increasing its reliability, capability, and capacity. Conventional electronics, with its separate functioning parts, has led to the micromodule—which achieves a density of a million parts per cubic foot. Beyond that looms integrated electronics, wherein one small crystal is designed and made to perform many different electronic functions. Thus far, some parts of digital-computer circuits have been made, by integrated-electronic techniques, with a density of one hundred million parts per cubic foot. This growing confluence of circuitry, devices, and materials requires technical men who can grow in knowledge, understanding, and creativeness in all three fields.

The electronics industry has provided a source of nourishment for continuing growth by custom-making new electronically active materials to satisfy the changing demands of its customers. Additional nourishment for growth could be, and probably will be, provided by custom-making other materials to replace those that are vital and presently unsatisfactory.

The writer would be pleased to receive, from readers of the RCA ENGINEER, suggestions as to areas wherein improvement in materials could substantially increase RCA's growth.



H. W. Leverenz
H. W. Leverenz
Director of Research
RCA Laboratories

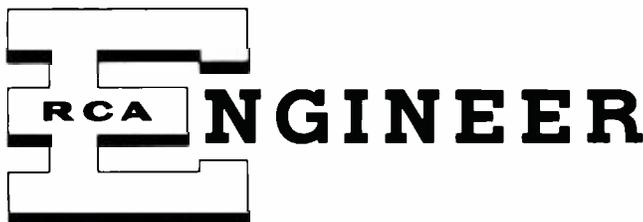
CONTENTS

| | | |
|--|--|----|
| Second RCA ENGINEER Readership Survey..... | P. C. Farbo and J. M. Cook | 2 |
| Materials Research..... | Dr. R. W. Peter | 4 |
| Effect of Crystalline Electric Fields on the Magnetism of the Magnetic Oxides..... | Dr. P. J. Wojtowicz and P. K. Baltzer | 10 |
| New Ferrites for Electronics..... | H. Lessoff, Dr. W. J. Croft and J. H. McCusker | 14 |
| Development of Square-Loop Ferrite Magnetic Memory Cores..... | J. J. Sacco, Jr. | 16 |
| Electroluminescent Phosphors — Gateway to a New Dimension in Lighting..... | J. P. Stanavage | 20 |
| Photoconductive Materials..... | Dr. G. S. Briggs and W. M. Kramer | 24 |
| Photoconductivity..... | Dr. R. H. Bube | 28 |
| Solid-State Analog of the Vacuum Triode..... | Dr. W. Ruppel and R. W. Smith | 33 |
| Dielectric Ceramics in Tubes..... | T. F. Berry and W. J. Koch | 36 |
| A New Approach to the Control of Cathode Alloys..... | Dr. I. F. Stacy and C. W. Horsting | 41 |
| Radiotracers in Parts-Cleaning Evaluation..... | M. N. Slater and Dr. D. J. Donahue | 44 |
| Conductors From Nonconductors — Adhesives, Coatings, Plastics, Papers, and Rubbers..... | Dr. L. H. Cutler | 48 |
| Recent Developments in Printed Wiring..... | Dr. O. T. Black | 51 |
| Materials and Processes For the Micromodule..... | C. Eddison | 52 |
| Ceramics and the Micromodule..... | Dr. B. Schwartz and Dr. H. Stetson | 56 |
| Patents Granted..... | | 59 |
| Pen and Podium..... | | 60 |
| Engineering News and Highlights..... | | 62 |

VOL. 5, NO. 4 • DEC. 1959-JAN. 1960

Copyright 1960
Radio Corporation of America
All Rights Reserved

PRINTED
IN
U.S.A.



Editorial Advisory Board

- E. I. Anderson, Chief Engineer,
RCA Victor Home Instruments
- J. J. Brant, Director, Personnel
- C. C. Foster, Mgr., RCA REVIEW
- M. G. Gander, Mgr., Engineering,
RCA Service Co.
- Dr. A. M. Glover, Vice President,
Semiconductor and Materials Division
- C. A. Gunther, Chief Defense Engineer,
Defense Electronic Products
- J. Haber, Director, Community Relations
- W. C. Morrison, Mgr., Engineering Plans &
Services, Industrial Electronic Products
- J. C. Rankin, Mgr., General Employment
- H. E. Roys, Mgr., Engineering,
RCA Victor Record Division
- D. F. Schmit, Vice President, Product Engineering
- Dr. G. R. Shaw, Chief Engineer,
Electron Tube Division
- C. M. Sinnett, Director, Product Engineering
Professional Development
- S. Sternberg, Chief Engineer,
Astro-Electronic Products Division

RCA ENGINEER Staff

- W. O. Hadlock, Editor
- E. R. Jennings, Assistant Editor
- Mrs. M. A. Suckow, Editorial Secretary
- J. L. Parvin, Art and Production
- J. O. Gaynor, Photography

Engineering Editors

- K. A. Chittick, Mgr.,
Engineering Administration,
RCA Victor Home Instruments
- C. A. Meyer, Mgr., Commercial Engineering
Technical Services, Electron Tube Division
- C. W. Sall, Mgr., Technical Publications,
Industrial Electronic Products
- L. A. Thomas, Mgr., Technical Services,
Astro-Electronic Products Division
- F. D. Whitmore, Technical Publications
Administrator, Defense Electronic Products

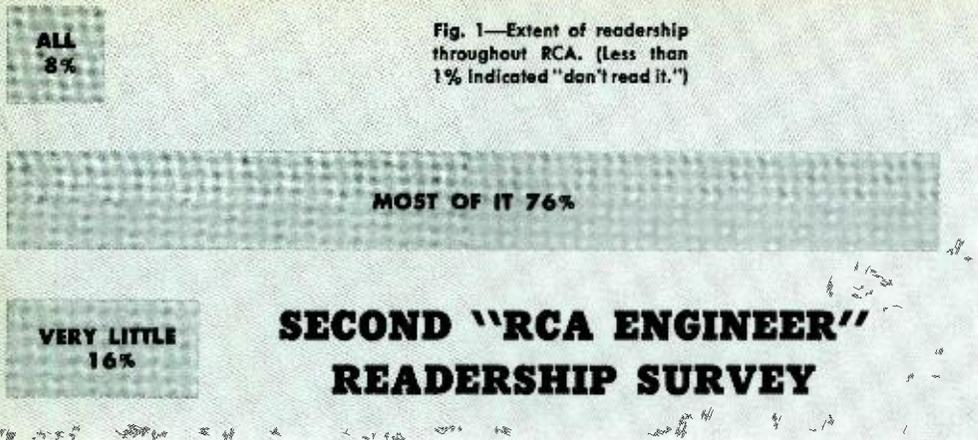


Fig. 1—Extent of readership throughout RCA. (Less than 1% indicated "don't read it.")



PATRICK C. FARBRO received his A.B. and M.S. degrees in psychology from the University of Tulsa (1947) and Purdue University (1948) respectively. He has also completed post-graduate work at Temple University and Institute of Pennsylvania Hospital. His occupational experience includes work as a graduate teaching assistant in psychology at Purdue University, 1947-1948; Personnel Research Analyst, RCA Victor General Office, 1948-1949; Employment Supervisor, Lancaster Plant, 1949-1951. In 1951, Mr. Farbro was appointed Manager, Personnel Research, RCA Staff; in 1957, Manager, Training and Personnel Research, RCA Staff; and in 1959, Manager, Professional Personnel Programs, RCA Staff. Mr. Farbro is a member of the American Psychological Association, the American Association for the Advancement of Science, the American Society of Training Directors, the International Association of Applied Psychology, and Sigma Xi.

This is the second readership study made of the RCA ENGINEER. The first study was made in 1956 in the second year of the journal's publication and has since that time helped to guide the editorial decisions to achieve the aim of the publication—a magazine "by and for the RCA engineer." This second study is an attempt to assess the acceptance and value of the magazine among RCA engineers and to guide future editorial decisions.

P. C. FARBRO, Manager and **J. M. COOK, Administrator**
Professional Personnel Programs, RCA Staff and *Personnel Research, RCA Staff*

A QUESTIONNAIRE WAS distributed with the Feb.-Mar., 1959 issue of the RCA ENGINEER asking that it be answered and returned anonymously to the editor. A total of 5,769 questionnaires were sent out; 905 questionnaires were returned—a 16-percent return, generally considered good for mailed readership surveys.

Several findings support the conclusion that the RCA ENGINEER is a good publication and is acceptable to the engineers at RCA. Of the 905 who returned their questionnaires, only one person said he didn't read the magazine. Eighty-four percent read "all" or "most" of the magazine.

Fig. 1 shows how the readers answered the item, *Check one category that best describes the extent of your readership.*

Also important to consider is the variation among various subgroups to see if one publication can be written successfully for a complex organization engineering and researching in diverse fields of entertainment products, industrial equipment, defense systems and space devices.

The publication seems to be applicable to this audience diverse in the areas in which they work as shown by Table I.

MAGAZINE BALANCE

A majority of the engineers indi-

cate that the balance between technical and nontechnical information is about right to suit them. In answer to the item, *Balance is satisfactory or unsatisfactory*, 88 percent indicated they were satisfied with the relative emphasis given to technical and nontechnical articles. This is common to the various operating units of the company as may be seen from Table II.

INTEREST IN CLASS OF ARTICLE

One item instructed the engineer to *Please rank the classes of articles in order of their interest to you (1, 2, 3, 4 and 5).* The classification of articles and their rank order of interest was as follows:

1. *Semitechnical* (Generalized papers on technical subjects)
2. *Technical* (Descriptions of design techniques, mathematical analyses and scientific papers on specific technical subjects)
3. *Editorials, Professional Information and Business Planning* (Orientation of engineer in his company and in his society. Economics of the Corporation and case studies on interdepartmental projects)
4. *Engineering Activities, Engineering Services and Plant Facilities* (Descriptions of engi-



JOHN M. COOK received his M.S. in industrial psychology from the University of Minnesota in 1951. He spent one year as a student counselor in the Minnesota Institute of Technology before coming to RCA as a personnel specialized trainee. He worked in Camden Engineering Employment and was Manager, Engineering Training and Personnel Studies prior to his present position as Administrator, Personnel Research, RCA Staff. Mr. Cook is a member of Phi Beta Kappa, the American Psychological Association, and the Division of Industrial and Business Psychology.

- neering functions at various plant locations)
5. *Magazine Departments* (Patents Granted, Pen and Podium and News and Highlights)

Although *Engineering Activities* and *Magazine Departments* were ranked lowest, there was evidence of enough interest to warrant their continuation.

"IMAGE" OF THE MAGAZINE

Forty-three statements about the magazine were used in the study which asked the respondent to answer

by checking if he *strongly agreed*, *agreed*, was *neutral*, *disagreed*, or *strongly disagreed* with the statements. From the responses to these items it is possible to develop a "composite image" of the magazine, as viewed by its readers.

These statements were scored by giving a weight of +2 or -2 if the person checked *strongly agreed* or *strongly disagreed*, respectively, in responding to the statements; +1 or -1 if the person checked *agreed* or *disagreed*, respectively, to the statements. A weight of zero was given to the neutral responses.

The image of the magazine described below is made up of those statements which reflect the opinion of more than one-half of the respondents and are listed in order of the strength of the engineers' feelings based on scores, as described.

This image can be considered to represent the feelings of the engineers in all the major operating units, since there is a high degree of agreement among the operating units. Evidence for this is that the correlation of each major operating unit's scores with total corporation scores ranged from 0.99 to 0.67 (median 0.87) where a correlation coefficient of 0.28 would be significant at 1-percent level of confidence.

In the "image" (see Table III), statements are listed in order of the strength of feelings of the respondents.

AUTHOR VOLUNTEERS

Another indication of the acceptance of the RCA ENGINEER is the interest indicated in the publication through volunteer authors. Through the question, *Would you write or co-author an article for the RCA ENGINEER?*, over 400 (close to one-half of the respondents) answered affirmatively. In addition, approximately one-half the respondents suggested titles or ideas for articles that would interest them.

Suggestions for articles range all the way from administrative systems, and managerial concepts and techniques to highly technical subjects and review articles describing a complete product line or research and engineering effort. These are on file in the office of the Editor of the RCA ENGINEER and will be used in planning future issues.

TABLE I—Percent of Readers Who Read "All" or "Most" of the RCA ENGINEER by Major Operating Unit

| | | | |
|--------------------------|--------|--------------------------|--------|
| IEP | 85.1 | Tube | 85.6 |
| DEP | 83.0 | TV | 100.0 |
| International | 100.0* | NBC | 100.0* |
| Laboratories | 79.3 | RCA Communications | 100.0* |
| Radio & "Victrola" | 90.9 | RCA Staff | 71.4* |
| Semiconductors | 86.6 | Records | 33.3* |
| Service Co. | 100.0 | AEP | 70.8 |
| TOTAL — | | 84% | |

*Response too small for reliable estimate.

TABLE II—Percent of Readers Who Indicate Satisfaction With The Balance Between Technical and Nontechnical Articles by Major Operating Unit

| | | | |
|--------------------------|--------|--------------------------|--------|
| IEP | 86.9 | Tube | 89.4 |
| DEP | 88.0 | TV | 95.2 |
| International | 100.0* | NBC | 80.0* |
| Laboratories | 87.2 | RCA Communications | 0 * |
| Radio & "Victrola" | 90.9 | RCA Staff | 100.0* |
| Semiconductors | 85.2 | Records | 75.0* |
| Service Co. | 83.3 | AEP | 87.0 |
| TOTAL — | | 88% "Satisfactory" | |

*Response too small for reliable estimate.

**TABLE III—Readers' "Image" of the RCA ENGINEER*
(Statements in Order of Strength of Response)**

The RCA ENGINEER places importance on the engineer as a vital link in the Corporation's progress.

The RCA ENGINEER is valuable to the experienced as well as the younger engineer.

The color covers are in keeping with the dignity of the engineering profession.

The interest and reputation of RCA and its engineers are increased by the journal.

Paragraph subheadings and explicit captions are good.

The editors do a thorough editing job.

The RCA ENGINEER is helpful in furthering the engineers' insight into RCA as a Corporation.

There should be more papers by engineering managers and top management on plans and objectives.

The publication helps the company's engineers to be better informed, thus enhancing job performance.

The RCA ENGINEER is satisfactorily meeting its published objectives.

There should be more papers devoted to business planning, economics and company objectives.

The journal has a professional atmosphere that engineers recognize and appreciate.

The RCA ENGINEER is especially valuable to the younger engineers.

All engineers have an equal opportunity to write articles for the journal.

The RCA ENGINEER encourages "professionalism" in engineering.

Engineers like to show the RCA ENGINEER to their guests and visitors.

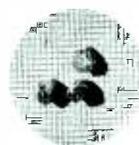
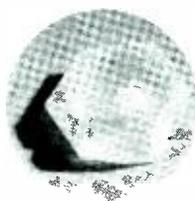
The RCA ENGINEER is a good means for recruiting engineers.

The RCA ENGINEER emphasizes the importance of interdepartmental cooperation on engineering programs.

The *Pen and Podium* section is a good reference source.

The publication encourages engineers to write.

* Made up of statements reflecting opinion of more than half of the respondents.



Dr. ROLF W. PETER received the M.S. in Electrical Engineering in 1944, and the Ph.D. in Radio Engineering and Physics in 1948 from the Swiss Federal Institute of Technology in Zurich, Switzerland. From 1946 to 1948 he was Assistant Professor of Radio Engineering at the Swiss Federal Institute of Technology. In 1948 he joined RCA Laboratories in Princeton, N. J. He was first engaged in traveling-wave amplifier research. From 1953 until 1957, he supervised the microwave and gaseous electronics research group. Since 1957 he has been Director of the Physical and Chemical Research Laboratory. Dr. Peter is a Member of Sigma Xi and of the American Physical Society, and a Fellow of the Institute of Radio Engineers.

MATERIALS RESEARCH

by

Dr. R. W. PETER, Director

Physical and Chemical

Research Laboratory

RCA Laboratories

Princeton, N. J.

THE EXPLOSIVE RISE of electronics from fiftieth place before the war to fifth today in American industry seems intimately related to the equally fabulous rise to importance of materials research and development during the same period. The general trend of this development in electronics is reflected in statistics of RCA Laboratories. When the Laboratory was started in 1942, only half a dozen scientists were involved in studies on materials, about half of them chemists. In 1959, about one quarter of the members of the Technical Staff are closely connected with materials research, and about half of those are chemists, metallurgists, and ceramists. These scientists are studying and trying to improve a vast number of materials, from insulators to superconductors. Of all areas of research at the Laboratories, materials research has expanded the most.

SPOTLIGHT ON MATERIALS RESEARCH

Why has the field of materials research and the need for new materials so sud-

denly gained this pre-eminent importance? Dr. A. B. Kinzel, in his opening address at the 1959 Navy *Materials Symposium*, pointed to the core of the situation: The cry for better materials is as old as engineering itself. However, in earlier times, the engineer who cried didn't know how far materials, such as steel, might be improved and, therefore, didn't wait for any improvements which in time came along. Today, by virtue of a better scientific training in the engineering education and also due to the influx of scientists into the sophisticated engineering areas, the engineer knows of the potentialities of materials, requests improvements, and waits for them. This puts an unprecedented pressure on the respective materials research groups. Success of their research now often becomes the key to the success of a whole engineering project of which the ultimate goal is based upon projected materials advances.

The main areas of research in RCA Labs are shown in Fig. 1: *materials* (and phenomena), *devices* (and components), *apparatus* (and circuits), and *systems* (and particularly, sub-systems). Each area critically depends on the area above, upon which the spotlight is focused when it is in trouble, until, at last, the spotlight stays and rests upon the materials group. As an illustration, let's look at a project which aims at creating a super-high-speed computer system. After eliminating optimum systems engineering as insufficient for achieving the task objectives, the search was after new super-fast switching and computing devices. Of the many possible solutions uncovered by the device research people, the tunnel diode shall be singled out. In spite of its outstanding capabilities, its frequency response has to be further improved, and this has to be done by improving the material. Presently, the spotlight is still on the semiconductor



The author, Dr. R. W. Peter, and Dr. R. E. Michel observing electron spin resonance in a paramagnetic crystal. Inset are some crystalline forms of important electronically active materials.

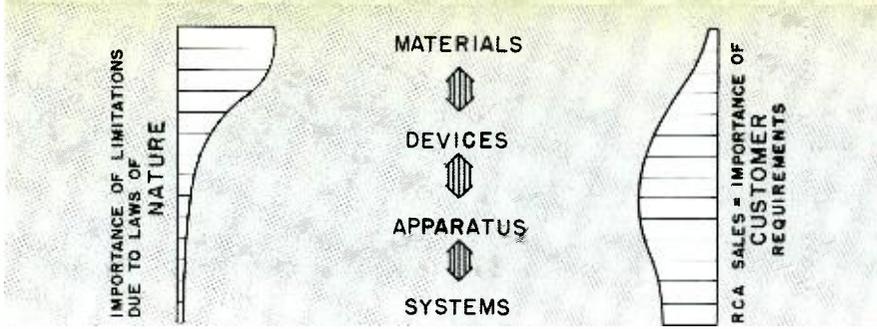


Fig. 1—The four main areas of research at RCA Laboratories. In the downward direction, the areas increase in complexity, each one depending crucially upon the preceding ones as building blocks. The left curve shows the relative importance of the limitations imposed by the laws of nature. Materials research is most-directly limited by nature, while progress in device research is impeded by imperfect materials much more than by the natural

laws (such as the finiteness of velocity of light). The right curve indicates the importance of the requirements imposed by the customer, expressed by the distribution of RCA sales in the different areas. RCA's business in materials is negligible; materials research consequently is aimed more at improving devices, rather than at the outside materials customer.

research group, which has to find a new way to greatly enhance the activator density in germanium for this purpose.

EVOLUTION OF MATERIALS RESEARCH

Even before the Laboratories were formed in 1942, materials development groups were responsive to the needs of apparatus and devices engineering groups in various Divisions of the Company. RCA's prime business in the pre-war period was in communication, radio, and phonograph, and the supporting materials work included most every component of a vacuum tube—cathode coating, metals, glass, and glass-to-metal seals. When the Labs were established, some of the most basic and critical materials problems transferred to Princeton: studies on dielectrics, phosphors, and dark-trace materials. In time, the materials program was aimed more and more at understanding and improving electronically *active* properties of solids, such as emission, luminescence, photoconductivity, and magnetism. The primarily *passive* aspects of materials, such as mechanical and chemical properties—tensile strength, elastic constants, specific heat, diffusion of gases through solid, chemisorption—were primarily studied in the Divisions materials groups as their more or less immediate needs demanded, just as were most of the linear electrical properties—such as ohmic conductivity, dielectric constant, permeability.

The general trend toward optimization and miniaturization of each individual part of electronic devices, however, has recently brought to light the need for more investigations into the passive properties of important materials. The aim of *Integrated Electronics* is to concentrate all functions of previous "circuits", including active and passive aspects, in one unit with minimal dimensions. Active areas with transistor-like properties will be integrated with passive, resistive, capacitive, or struc-

tural supporting areas of the material unit. Basically, of course, all properties of a material, whether called "active" or "passive", depend upon its atomic and electronic structure.

Fundamental physical studies, therefore, provide the foundation from which more detailed investigations can be launched in either direction.

During the past two years, research investigations have been started in the Laboratories into some primarily passive materials properties. Studies such as the following are representative: heat transfer between hot surfaces, heat conduction and other thermal properties in metals and insulators, dielectric behavior of insulators (including electric breakdown), deposition of inert surface layers on semiconductors, stable resistive films, organic materials to bind magnetic particles on a tape or electroluminescent particles on a panel, and mass spectrographic study of diffusion and evolution of gases from solids.

MATERIALS CLASSIFICATION AND SOME CONCLUSIONS

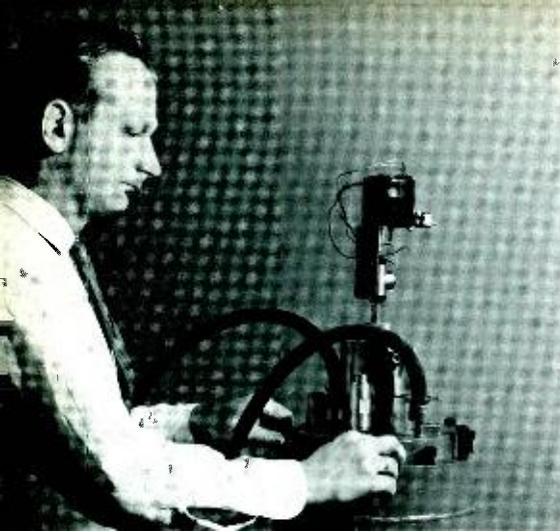
The wide range of materials studied at the Laboratories may be classified in many different ways. In Fig. 2, the order

is according to the energy-band gap of the material. It is inversely related to the conductivity as indicated. The conductivity scale also seems to give an approximate indication of the degree of the existing physical knowledge on any of these materials and the related phenomena! This is a rather astonishing fact, considering that some of the earliest known and most extensively studied materials head the list, such as insulating and luminescent materials, followed by photoconductors. Although scientific studies on luminescence go back to the 16th century, the basic complex mechanisms involved are still very much less understood than semiconductivity, a relatively recent addition to the list of observed materials phenomena.

The reason for this peculiar situation lies in nature itself. It has been said that every additional electron volt of energy gap increases by at least an order of magnitude the difficulty to synthesize a crystal of equal chemical and structural purity. Semiconductors are distributed near a 1-ev gap, visible photoconductors around 2 ev, phosphors group around 3 ev, and their order of complexity increases accordingly. In addition, the difficulties for the synthesis chemist or metallurgist further grow when he progresses from elemental crystals, such as Ge or Si, to binary compounds, such as InP or CdSe, or ternary compounds, such as AgFeTe₂. Solid-state theory at present is barely able to explain adequately "from first principles" the phenomena found in highest-purity Column IV crystals, Ge and Si. This standard of purity requires the content of foreign atoms to be less than one in a billion atoms, and the dislocation density to be below 100/cm.² Progress toward better understanding of materials, therefore, is closely linked to the availability of chemically and structurally purer materials.

Fig. 2—Materials are classified here according to their energy bandgap. The high-bandgap materials on top are good insulators, the zero-bandgap materials (metals) on the bottom are the best conductors. Materials in the right-hand column show spontaneous polarization, while the materials in the main column do not show this phenomenon. Generally speaking, materials are more complex and, therefore, less understood, the larger their energy bandgap.

| Energy Band-gap | Conductivity (in darkness) | M A T E R I A L S | |
|-----------------|----------------------------|---------------------------|-------------------------|
| High | Negligible | Dielectrics (Insulators) | Ferroelectrics |
| | | Phosphors | |
| | | Photoconductors (visible) | |
| | | Paramagnetic Materials | Ferrites |
| | | Emitters | |
| | | Photoconductors (IR) | |
| | | Semiconductors | |
| | | Thermoelectrics | |
| | | Metals | Metallic Ferromagnetics |
| Low | High | | |
| Zero | Infinite | Superconductors | |



Dr. A. G. Fischer adjusting a high-temperature, high-pressure reaction furnace for use in crystal growth.

THE THREE MAIN FACES OF THE MATERIALS MAN

Before discussing some specific materials research activities, consider the main problem the materials scientist is faced with—be he chemist, physical chemist, metallurgist, or ceramist. The device man requests from him improvement of a certain property or phenomenon in a material (keeping all the others the same, of course!). For example, he may be asked for a material with higher carrier mobility at elevated temperature for improved, heat-resistant semiconductor devices.

The first and main step the chemist has to face is the selection of the material which might best provide the optimum combination of desired characteristics. At his disposal is the whole periodic table of some 90 elements to play with. Combining two elements at a time leads to over 4000 combinations, of which a larger fraction are mixtures and a smaller fraction are actual compounds. If he also considers ternary compounds, built up of three elements, the number of materials he has to select from grows to over 100,000. The task in its full aspect is obviously fantastic. Besides some general rules and the chemical annals and handbooks, good horse-sense and infinite patience in trying out hundreds of variations are the best aids to the searching chemist.

There will come a time in the future when a fast computing machine will be able to supply physical data, such as bandgap and carrier mobilities, on a large number of simple compounds. The machine then will select the one or few best suited materials, e.g. GaAs as the preferred binary semiconductor in our example (what the best ternary compound is, we still don't know!). We have such an ambitious theoretical program active at the Labs, but do not expect to be waiting for the theorist to provide the choice selection for some years to come!

Even at that time, the other two most demanding tasks still remain with the materials scientists: the ultimate purification of the choice material, and the controlled alloying, "doping," and activating. The attitude and the talents of the scientist involved in purification have to be similar to those of a Sherlock Holmes! The killers he is after are unwanted impurities and defects in the materials. In the example of GaAs they appear to be as tough and elusive as the criminals in a perfect murder.

The third job the materials man has to perform is the one of an artist. Highly sensitive to the resulting change, he alloys the purified elements and compounds and, finally, introduces the active impurities and "dopes." Sensitive measurements guide him step-by-step in this final endeavor of activating a piece of purified material to bring out the desired particular quality or phenomenon. Ge or GaAs, for example, may be activated to become basic material for a transistor, for a tunnel diode, or also for an infrared photosensitive detector.

The conclusion is that, symbolically speaking, the "materials man" has to have three faces to carry out his complex task of creating a new material with the desired characteristics to order. He has to be a "cook" with good horse-sense and much experience, as well as many recipe books, a "detective" with imagination and analyzing power, and an "artist" with sensitivity and thorough knowledge.

In all three areas, the materials man depends upon sophisticated apparatus and often he is no better than his equipment. Besides standard chemical and furnace facilities, a speck-pure and a high-pressure lab are at his disposal at the Laboratories. At present, the most modern arc-image furnace and other facilities for high-temperature synthesis are being installed, opening an entirely new area of possible materials synthesis to RCA. Similarly, the most advanced equipment for sophisticated measurements is available. Examples are the several 12" Varian magnets, spin and nuclear magnetic-resonance equipment, the most sensitive existing susceptibility balance, and many others.

ORGANIZATION OF MATERIALS RESEARCH

The scientists with all three faces mentioned above are very rare. This is why materials research is most successfully carried out by teams, which together comprise the talents of a "cook", a "detective" and an "artist". They are recruited from many professions: chemistry, metallurgy, ceramics, both experimental and theoretical physics, and mathematics. In close cooperation, they pool their efforts in synthesis, measurement, analysis, and theory. A typical materials research group is shown in Fig. 3. As is schematically shown, the materials research team in the center depends in an intricate way upon cooperation with other groups and individuals in the Laboratory and in the Product Divisions.

The "Materials Analysis" group cooperates on the determination of the elemental components, impurity traces, and atomic structure of a material. Physical analytic methods—such as X-ray, ultra-violet, light, and infrared spectroscopy, electron microscopy, and mass-spectrometric studies—are complemented by wet chemical analysis methods, in part very sophisticated. Super-sensitive trace-element studies are carried out with radio-isotopes. The Industrial Reactor Laboratory research reactor, located near Princeton, where RCA as

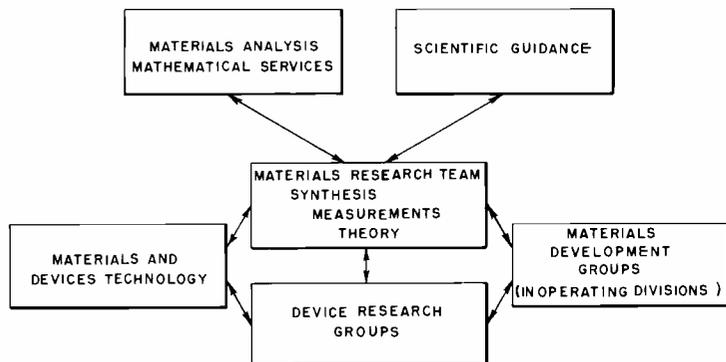


Fig. 3—Organization of materials research. The materials research team is closely cooperating with groups which can provide the analytical services and scientific guidance on the one hand, and with groups, either inside the Labs or in an Operating Division, which can assist in materials development and sampling. The main customer of all materials efforts are the respective devices research groups.

co-owner occupies a permanent laboratory, will permit carrying out analysis by neutron activation and diffraction. The "Mathematical Services Group" provides programming and computing services. Besides running its own IBM-650 computer, this group also has access to much faster IBM-704 and 709 machines when needed.

Of great significance for prosperous and successful materials research is the general scientific stimulation and guidance provided by a number of outstanding scientists with international reputation in their fields. Some of these experts are members of a particular materials group, many of them are in what we call the "General Research Group", and some are members of the small research Laboratory maintained by RCA in Zurich, Switzerland. As their main function is to advise and consult, these experts have an obligation to stay on top of their respective scientific field and, consequently, have to select and direct their work accordingly.

Small companies usually depend upon outside consultants. University professors mostly, as their scientific advisers. For a large laboratory, such as ours, the advantages of having leading scientists located right in the Laboratory whenever a profound problem arises are very great. They provide an ever-present critical advisory and sounding board for problems and novel ideas. Sometimes they save the Company large amounts of dollars by proving that a proposed project is as doomed to fail-

ure as one on perpetual motion. Less tangible than their direct, short-term economic effect are the contributions of these top scientists to the stature of the Laboratories and RCA as a whole in the scientific world. They open the doors for us to other research institutions. They hear about the scientific news before it appears in print and may give, thereby, a decisive head start in some rapidly changing field.

The "Materials and Device Technology" group assists the materials research group in supplying most advanced samples of new materials to the device researcher by duplicating achieved materials synthesis and providing him with large enough samples. Often a "Materials Development Group" in a Product Division may take the function of the device man's "new-materials supplier". A Lancaster group, for example, duplicates and produces our new phosphors and photoconductors in large-enough batches for the device groups at the Laboratories to carry out their experiments on novel photoelectronic devices.

THE I.Q. OF A RESEARCH LAB

The intelligence and inventiveness of an individual may be measured by some factor of merit, called "I.Q.", which shall not be defined in any detail here. This I.Q., it is known, does not only depend on selected special capabilities of an individual, like an indelible memory for names, but seems to be commensurate with the individual's capability to cross-correlate different,

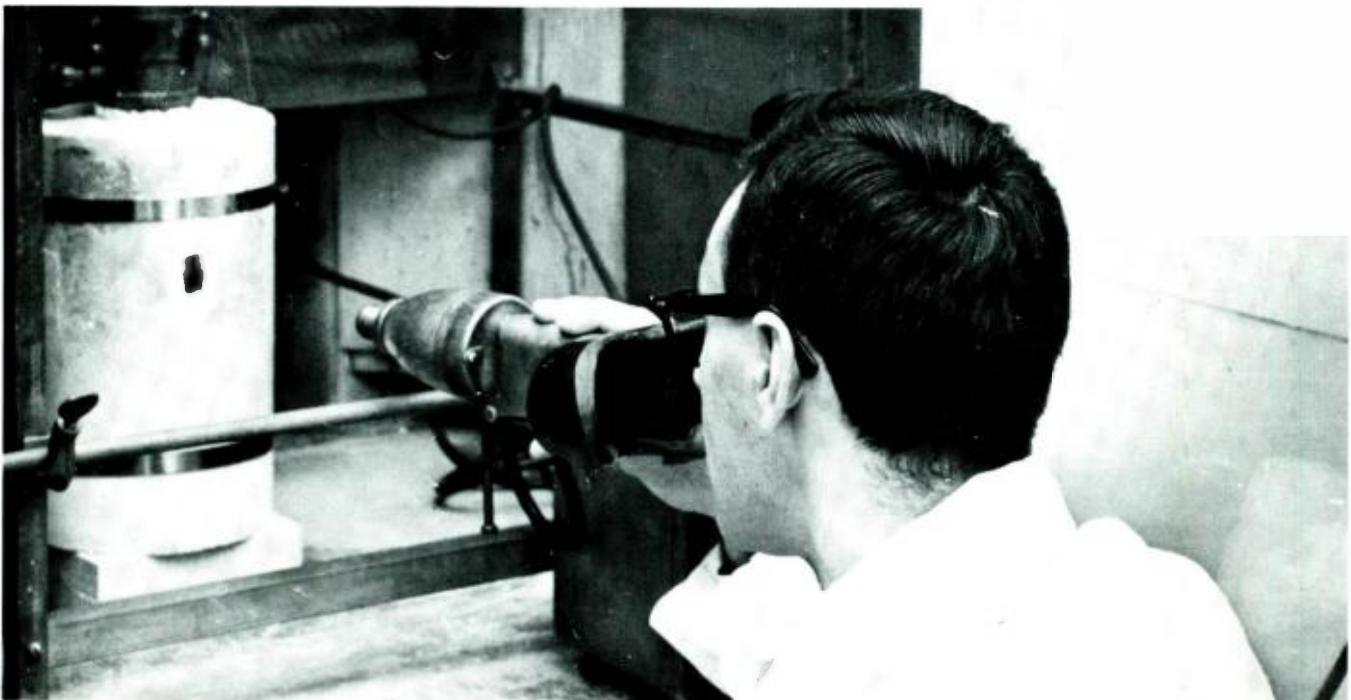


L. A. Zanani changing ferrite samples on a magnetometer, which measures the magnetic movement of materials.

not *a priori* related areas of experience or talent. Post-mortem brain studies on individuals with eminent intelligence revealed, as the only perceptible difference, a larger than normal number of nerve connections *between* individual brain areas.

Similarly, a social organism, or organization, built up of many individuals—such as a research laboratory—has a collective intelligence which may be expressed by an I.Q. factor. In a highly centralized authoritarian organization, the collective I.Q. may be

M. Kestigian measuring optically the temperature of crystal boules in a Verneuil Furnace.



not much larger than the I.Q. of the man on top. In a successful research lab, it is considerably higher than any individual member's I.Q.

I submit here that, just as in the physiology of the human brain, a laboratory I.Q. increases with the number and quality of the cross-linkages between individuals, groups, and sections inside the lab and out. Basically, our Laboratory is organized by functions, as shown in Fig. 1. Each area roughly corresponds to a "Section" or "Laboratory" in the RCA Laboratories. Linkages within each Section grow easily and naturally as they follow not only lines of authority, but lines of common scientific background and interests. Much less "self-organizing" are the linkages between Sections, along project lines. These project connections—some shown in Fig. 3—change dynamically with the character of the projects. Formal and informal meetings and discussions between individual scientists are the basis of these cross-linkages. To further assist in establishing these "vertical" linkages, "Project Coordinators" are appointed and endowed by the Director of Research with special authority and responsibility for the organization and technical performance of a project group. Our High-Temperature Semiconductor project is an example. The "Project Coordinator" usually has direct-line authority over a part of the activity and advisory or indirect authority over the rest. The Laboratories collective intelligence, inventiveness and general effectiveness—in short its I.Q.—is greatly dependent upon these projects-oriented connections, and much effort is spent to nurture them and let them grow.

RECENT ADVANCES IN MATERIALS RESEARCH

Finally, I would like to illustrate the effective functioning of our materials research activity by pointing to a few striking recent advances spearheaded by research teams at the RCA Laboratories.

They serve as representative examples, as completeness is impossible here. Several papers in this RCA ENGINEER issue provide more-detailed testimony.

Major advances were recently made at the Laboratories in perfecting phosphors and photoconductors, the photo-electronic materials which are basic to most image-detection, -reproduction and -storage devices.

In the phosphor, or "light-generation," domain, dramatic improvements

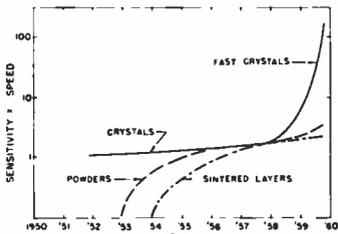


Fig. 4—Progress in photoconductor performance. After only nominal progress during the two preceding years, a breakthrough has recently been achieved in crystals. The yield of fast crystals, however, is still small (about 25%).

were made in electro-luminescent and in cathode-luminescent films. Fig. 4 indicates the increase in efficiency of various phosphors used for converting electricity into light. The steep and continued efficiency rise of electro-luminescent phosphor efficiency points to its imminent importance for many display and special lighting applications. It is quite conceivable that greatly improved electro-luminescent panels might ultimately become competitive with conventional means for general lighting. The efficiency of cathodoluminescent films rapidly approaches that of powder phosphors. Higher contrast and definition, and the possibility of color change by electron-voltage change promise possibilities for cathodoluminescent films in television and radar reproducer tubes.

Photoconductors are in an equally exciting period of major breakthrough. Recently, large possible increases in performance were predicted by theo-

rists at the Labs for photoconductors with the correct impurity content. During the past year, crystals with about two orders of magnitude higher performance factors were grown than ever known before, as shown in Fig. 5. Though an exceedingly difficult task, it can be assumed that eventually the same performance may be achieved in powders and sintered layers, which are required for most photo-electronic devices. Infrared photoconductors have been perfected to a similar degree during the past few years. Their spectral response can now be tailor-made to an amazing degree.

The phenomenon of space-charge-current flow, well known in vacuum tubes, was recently predicted and later measured in highly purified insulators, such as CdS. Initially considered no more than a particular aspect of photo-conduction, space-charge current flow has since been used for the first time in

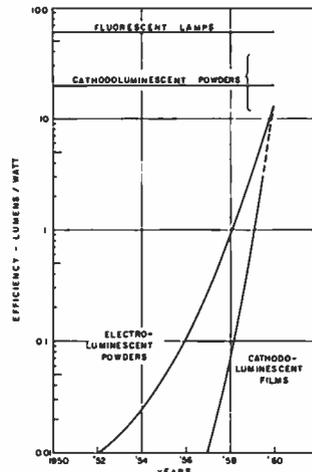
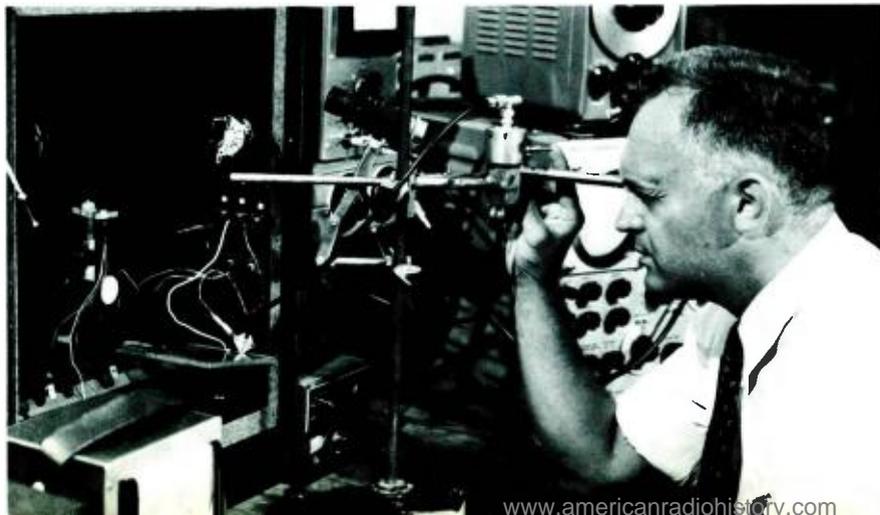


Fig. 5—Progress in phosphor efficiency. While photoluminescent phosphors (in fluorescent lamps) and cathodoluminescent powders (in kinescopes) showed only nominal improvements during the past few years, electroluminescence and thin-film cathodoluminescence are rapidly reaching competitive levels of light-conversion efficiency.

a solid-state analog to the vacuum-tube triode. Although still very much in its infancy, this high input-impedance device may herald a new class of "insulator devices" to reach importance as solid-state complements to the low-impedance semiconductor devices.

A newly built flame-fusion furnace was used to synthesize at high temperature the refractory paramagnetic crystals presently operating in the Lab's most versatile maser amplifier. Several types of non-linear materials, such as magnetics, dielectrics, and ferroelectrics, may be applicable to parametric signal amplification besides semicon-

R. W. Smith measuring photoconductive processes in single crystals.



ductor diodes. Basic material studies in these areas will provide new insight and possibly new solutions.

In all communications systems, signal amplification at any frequency from audio up to microwaves remains the pre-eminent function. Semiconductors still provide the basis for by far the most important solid-state amplifier devices. After an extensive search, GaAs was selected as the semiconductor material with the best combination of advantages. Its high carrier mobilities and high-temperature operating capability (up to 475°C) place it potentially far ahead of Ge or Si. A large team effort of "detective" and "artist" talent is being aimed at purifying and controlled doping of GaAs. The first operating GaAs transistor-type device was recently demonstrated, a major event in this field. Parametric and tunnel diodes prepared from GaAs have a higher frequency response and lower noise factor than any similar device made of Ge or Si. As mentioned before, the last word on the "ultimate" semiconductor has not been spoken yet. Search for better ternary compounds has led to two materials with very promising properties for tunnel-diode and thermoelectric applications. Still better ones may be uncovered.

Electronic conversion of radiation into electricity, without use of moving mechanical parts, open new possibilities

for our Company. The photovoltaic, thermionic, and thermoelectric principles are studied at the Labs as most promising and mutually complementary in their field of application. All three methods depend critically upon new materials for success. Our sizable thermoelectric materials effort has led as a first result to the most efficient low-temperature thermocouple—7-percent energy conversion at a temperature drop of only 300°C. Materials for thermoelectric cooling are quite different in composition from those specifically designed for power generation. The temperature range of operation is one of the main factors determining the best semiconductor mixture. For this reason, best generating materials will even vary in composition from the hot to the cold junction. Advances made during the past few years are evident from Fig. 6. The cooling efficiency of a refrigerator based upon a material with a figure-of-merit of 3×10^{-3} is about equal to that of a small, or about half the efficiency of a large, commercial mechanical refrigerator. Considerable improvements appear possible.

Information storage for computers and recorders is being achieved in ever-tinier specks of ferromagnetic and other materials. From magnetic cores, printed ferrite, and metal plates with microscopic holes, the trend toward higher and higher information-storage density

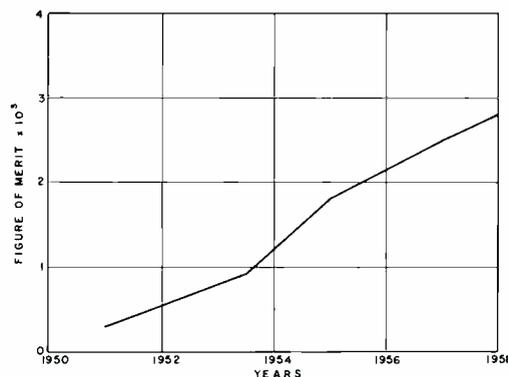


Fig. 6—Progress on the cooling efficiency of thermoelectrics, as generally expressed by a factor of merit. (Assumed is that the hot terminal of the thermocouple is at room temperature.) Using materials with a figure-of-merit of 3×10^{-3} , a thermoelectric refrigerator can be built to operate about as efficiently as a small or about half as efficiently as a large commercial mechanical refrigerator.

leads to magnetic tapes and films. Attempted improvements in ferroelectrics may some day make practical the use of those materials for certain switching and storage functions. Basic studies carried out on new superconductors and on the mechanism of switching will permit improving the design of novel cryogenic memory and storage devices.

SUMMARY

Materials are becoming more and more the key to progress in electronics. The demands for new materials increase rapidly. The complexity and sophistication of materials research are growing. Teams of scientists with required diverse talents appear to be best suited to handle the three-fold aspects of materials research. Long-range fundamental investigations of the basic properties of matter are important to provide broad scientific guidance in today's accelerated search for new and better materials. Close cooperation between different teams—particularly those involved in related materials and devices research—is essential. The quality and quantity of cross-linkages between groups—complementing the formal organization—relate directly to the laboratory's "I.Q."

During the past decade, RCA Laboratories scientists have contributed greatly to the science and technology of electronically active materials. Pioneering work has established RCA Laboratories in the eyes of the industry and the scientific world as one of the leading scientific centers of materials, especially solid-state, research. Our aim is to affirm this position by future contributions to RCA and indirectly to the materials sciences at large.

M. Abrahams operating the Instron tensile strength testing machine.



EFFECT OF CRYSTALLINE ELECTRIC FIELDS ON THE MAGNETISM OF MAGNETIC OXIDES

by

Dr. P. J. WOJTOWICZ and P. K. BALTZER

*Physical and Chemical Research
RCA Laboratories
Princeton, N. J.*

THE MAGNETIC OXIDES have become important in the field of electronics mainly because of their high electrical resistivity and the ease with which they can be prepared as ceramic materials. The major macroscopic properties of the magnetic oxides basic to their engineering performance are the magnetization, the anisotropy, and the Curie temperature. Such other properties as the permeability, the coercive force, and the B-H loop shape are describable in

terms of the above major properties. A knowledge of these characteristics is usually sufficient for the intelligent conception and design of useful magnetic and electronic devices.

The macroscopic properties such as magnetization, anisotropy and Curie temperature, however, are in turn the result of the individual and collective

properties of all the ions, magnetic as well as nonmagnetic, of which the substance is composed. To properly understand the behavior of magnetic materials, it is of the utmost importance to first understand the physics and chemistry of single magnetic ions, of their interaction with each other, and of their interaction with the crystal lattice in which they reside. Once an understanding of this information is obtained, it should be possible to predict the influ-

The visualization of atomic arrangements and electric field configurations in crystals is greatly aided by the use of "ball and stick" models of lattice structures. Here the authors, Dr. P. J. Wojtowicz (left) and P. K. Baltzer, examine a model of the Perovskite lattice, a structure commonly encountered in studies of magnetic oxides.

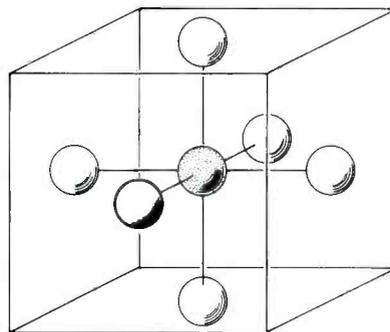
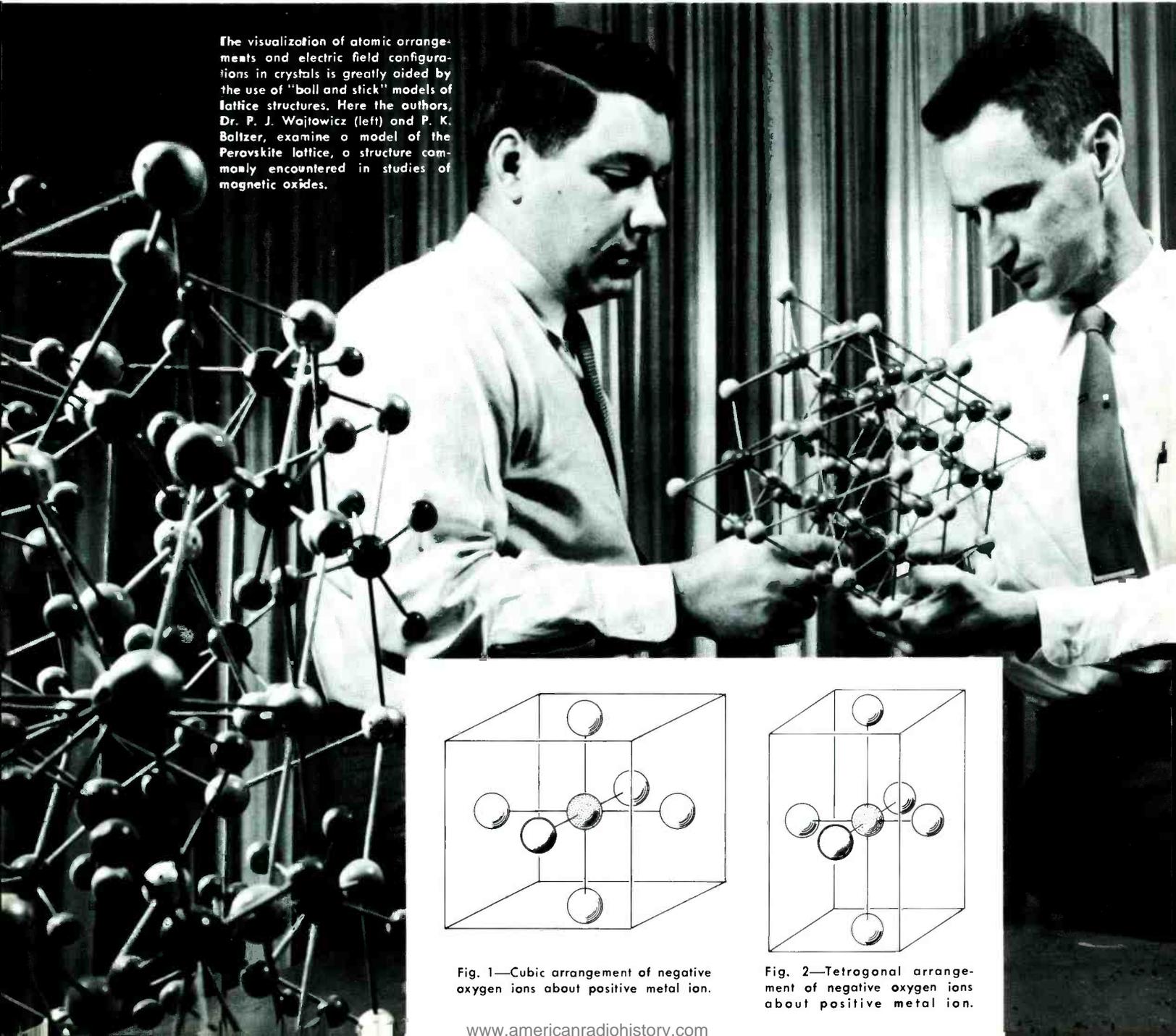


Fig. 1—Cubic arrangement of negative oxygen ions about positive metal ion.

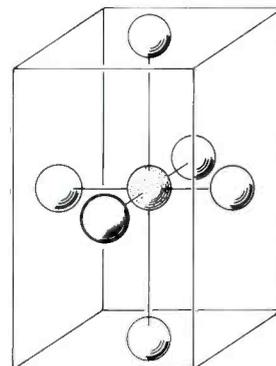


Fig. 2—Tetragonal arrangement of negative oxygen ions about positive metal ion.

ence of these microscopic interactions upon the properties of future magnetic oxides. The ultimate aim, of course, is to be able to specify the composition of materials that will satisfy the requirements of given specialized practical applications.

Within recent years, our understanding of the complex microscopic interactions within magnetic materials has been significantly advanced by the application of the crystal field theory. The success of the crystal field theory in explaining and predicting the magnetic properties of matter has in fact been so pronounced that it is now clearly apparent that the crystal-field point of view will become important to magnetism as the energy-band viewpoint is to semi-

conduction, photoconductivity, and luminescence. In this article we shall present a brief outline of the crystal-field point of view—what a crystalline electric field is, how it arises, some of its important properties, how its influence on magnetism comes about, and its impact on magnetic-material research. If at the end of this paper the reader no longer finds it incongruous that crystalline *electric* fields actually influence the *magnetism* of a material, then the purpose of this article has been fulfilled.

THE CRYSTALLINE ELECTRIC FIELD

An atomistic description of the macroscopic properties of the magnetic oxides requires a consideration of how such materials are constructed from their constituent ions. The positively charged iron-group metal ions and the negative oxygen ions are arranged in a regular periodic structure known as the crystal lattice. Since the crystal lattice is periodic, it is possible to describe it completely in terms of small, identical, elementary building-blocks called unit cells. The systematic repetition of unit cells in all three spatial directions then makes up the complete lattice of the material. The unit cell in turn is constructed from even simpler geometrical units such as that shown in Fig. 1. Depicted is the characteristic arrangement of six oxygen ions about a central metal ion found in most magnetic oxides. By the systematic packing of small numbers of such units, the various unit cells actually found in magnetic oxides may be constructed. An important aspect of these, is that all the positive metal ions are surrounded locally by negative ions only, and vice versa.

Now, since each ion possesses an electric charge and gives rise to an associated electric field, any one ion in the crystal lattice is bathed in the net electric field of all the surrounding ions. This net electric field experienced by each ion in the lattice is called the *crystalline electric field*. The condition for the mechanical equilibrium of the lattice demands that the net crystalline electric field vanish at the exact center of each of the ions. However, in the region of space immediately surrounding the geometrical center of the ions—the region in which the electrons orbit—the net field is nonvanishing. Thus, while the ions suffer no net electrical forces, the magnetic electrons thereof do actually experience instantaneous forces from the crystalline electric field.

The net electric field in the immediate vicinity of a positive ion is almost entirely due to that produced by the six negative ions locally surrounding it

(see Fig. 1); contributions from more-distant positive and negative ions in the lattice largely cancel and contribute little to the net field. The character of the crystalline electric field at a positive ion can therefore be simply discussed in terms of only the six nearest neighboring oxygens. The geometry of the field is therefore necessarily related to the geometric arrangement of the oxygens about the positive ion. In the arrangement depicted in Fig. 1, the oxygen ions are seen to lie in the faces of an imaginary cube surrounding the central positive ion. The geometry of this arrangement is clearly related to the geometry of the cube. The symmetry of the oxygen arrangement, and hence that of the resultant field, is therefore the same as the symmetry of the cube, that is, cubic symmetry.

The value of recognizing these symmetry properties will be illustrated by the following example. As we shall see later, one of the most important characteristics of the crystalline electric field is the location of the areas of maximum field strength. The areas of maximum field strength will be those in which the negative electrons of the central ion experience the greatest repulsive forces from the oxygens. The repulsive forces will be greatest along the lines drawn between the central ion and the oxygens shown in Fig. 1. Now, just as there are six equivalent faces in a cube, so must there also be six equivalent regions of maximum field strength. The areas of minimum field strength will be those in which the electrons suffer the least repulsive force. These areas will fall along cubic edges, explicitly avoiding the neighborhood of the negative oxygens. As there are twelve equivalent cube edges, so must there also be twelve equivalent regions of minimum field strength.

The cubic arrangement shown in Fig. 1 is the most symmetrical possible, but is not the one always found in nature. Quite often in the magnetic oxides, the tetragonal arrangement shown in Fig. 2 is found. Here the magnetic ion is still surrounded by six oxygen ions, but now two of the oxygens are more distant from the central ion than the other four. The equivalent figure in whose faces the oxygens now lie is a right-square prism. The symmetry of the crystalline electric field in this case is therefore the tetragonal symmetry of the right-square prism. The major consequence of this change in symmetry concerns the number of equivalent regions of maximum field strength. In Fig. 2, the faces of the prism are no longer all equivalent as in the cube. Thus, the six regions of

DR. PETER J. WOJTOWICZ

received his B.S. in Chemistry from Rutgers University in 1953, and the Ph.D. in Physical Chemistry and Physics from Yale University in 1956. He was a National Science Foundation Fellow at Yale, 1953-56. Dr. Wojtowicz joined RCA Laboratories at Princeton in August 1956 as theoretical physical chemist. Presently he is a member of the General Research Group and is responsible for theoretical investigations of the magnetic, thermal, and structural properties of magnetic materials. He is a member of the American Physical Society, Phi Beta Kappa and Sigma Xi.

PHILIP K. BALTZER

received the B.S.E.E. from Northeastern University in 1952 and the M.S. in Physics from M.I.T. in 1955. He joined RCA Laboratories, Princeton, N. J., in 1955 and since 1956 has directed the basic research on magnetic materials. He is responsible also for coordinating the applied research activities on ferrite materials involving the RCA Laboratories and the RCA Semiconductor and Materials Division. He is a member of the American Physical Society, Sigma Xi, Tau Beta Pi, and Eta Kappa Nu.

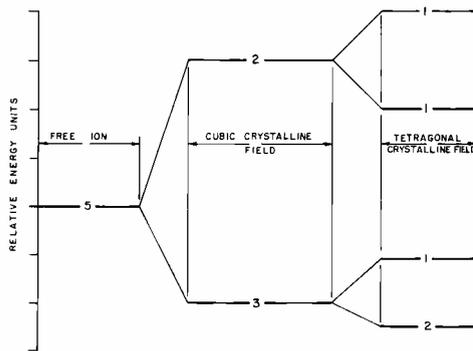


Fig. 3—Relative allowed energies of magnetic electrons in crystalline fields.

maximum field strength will also no longer all be equivalent. Reference to Fig. 2 shows that the four areas of maximum field strength associated with the lines drawn to the centers of the four equivalent vertical faces remain equivalent. The two faces at the top and bottom of the prism, on the other hand, are equivalent to each other but not to the remaining four. Thus, the areas of maximum field strength associated with the lines drawn to these faces will be equivalent only to each other but not to the previously discussed four. Furthermore, since the oxygen ions in these two faces are more distant from the central metal ion, the magnitude of the maximum field strength in these two equivalent areas will be less than that in the other four equivalent areas.

MAGNETISM OF IONS IN CRYSTALS

Magnetic ions derive their magnetic properties from just a few outer-orbiting electrons which we will call the *magnetic electrons*. The remaining inner-orbiting electrons and the nucleus do not contribute to the magnetism and may simply be thought of as providing a suitable carrier for the magnetic electrons. Now, each electron acts as a microscopic permanent magnet capable of assuming various orientations in space. This electronic magnet is popularly known as the electron *spin*. Within an ion, the magnetic electrons may have their spins aligned either parallel or antiparallel to each other. Two electrons with spins aligned antiparallel to each other are called spin-paired; the magnetic effect of paired spins cancel exactly and hence do not contribute to the magnetism of the ion. The net magnetic moment of an ion is just the sum of the parallel aligned spins of the unpaired magnetic electrons.

In order to understand and predict the magnetic moments of ions in crystals, it is necessary to take full account of the influence of the crystalline electric field in determining both the total number of magnetic electrons and the number of unpaired spins. The maximum number of magnetic electrons possible in the iron-group ions is ten. The

maximum number of unpaired spins is five; any increase in the number of electrons above five automatically requires spin-pairing. The actual numbers present will be those corresponding to the state of minimum electronic energy for the ion.

We must therefore consider how the crystalline electric field affects the possible energies of the magnetic electrons. In the free ion (that is, one *not* under the influence of electric fields), all the magnetic electrons present will be equivalent having the same allowed energy value. If, however, the ion is placed in a crystalline electric field of cubic symmetry the electrons will no longer be equivalent and two sets of allowed energies now prevail. Fig. 3 illustrates how the allowed energy level in the free ion is *split* by the cubic field. The depressed energy value corresponds to those electrons whose motion carries them predominantly into the regions of minimum field strength (discussed in connection with Fig. 1), while the raised energy value pertains to those electrons which predominantly orbit in the regions of maximum field strength. The numbers associated with the energy levels in Fig. 3 indicate that while as many as five unpaired electrons could have the same energy in the free ion, only three unpaired electrons may now possess the low energy value allowed in the cubic field, the other two possible being constrained to have the higher allowed energy value.

A reduction of the symmetry of the electric field to tetragonal symmetry (Fig. 2) causes further splittings in the allowed energy levels as depicted in Fig. 3. Since the regions of maximum field strength are no longer equivalent in this case, electronic motion in these regions also cannot be equivalent. The high allowed energy value of the cubic case therefore splits into two new levels. The higher energy corresponds to the motion of electrons predominantly in the plane of the four close oxygens, while the lower energy obtains for electronic motion along the line connecting the two further-removed oxygens. As indicated in Fig. 3, only single unpaired electrons may now possess the upper

energy values discussed. The lower energy level of the cubic case is also split, since the regions of field strength minima are also not equivalent in tetragonal symmetry, as can be seen by reference to Fig. 2. The very-lowest energy value corresponds to motion in regions near the edges at the top and bottom of the prism, while electronic motion in the regions near the vertical edges of the prism will give rise to a slightly higher energy value.

In Fig. 3, as well as in the preceding text, we have indicated the number of *unpaired* electrons that are permitted to have the various allowed energy values. Actually, twice these numbers of magnetic electrons may have these energies. But, when the additional electrons desire these energies they must pair their spins with those already present (thereby reducing the total number of unpaired spins). It would therefore seem that the ion could lower its total electronic energy in the field by pairing spins and requiring that all its electrons have the lowest allowed energy values. This would be so if it were not for the competing tendency of magnetic ions to possess as many unpaired spins as possible. The resulting energy and number of unpaired spins per ion will depend on the outcome of these two competing processes.

The application of the crystal-field point of view to the resolution of this problem will be illustrated in a number of examples that have been of concern in the magnetics research programs at the RCA Laboratories. There are two distinct mechanisms by which the number of unpaired spins may be altered through the agency of the crystalline electric field; these are (a) the valence-exchange mechanism, and (b) the spin-quenching mechanism. In the first mechanism the total number of magnetic electrons per ion is altered, this effect necessarily being accompanied by a change in the electric charge or valence of the ions involved. In the second mechanism the total number of magnetic electrons remains the same, but the number of spin-paired electrons is increased. Examples including both of these processes will be discussed in the following sections.

THE VALENCE-EXCHANGE MECHANISM

Many of the magnetic ferrites used in electronic technology today contain both iron and manganese ions. In those compounds where the combined valence of these ions is constrained to be five, the usual facts of chemistry tell us that these ions will coexist as Fe^{3+} and Mn^{2+} . Both Fe^{3+} and Mn^{2+} have five magnetic electrons. In the cubic crystalline fields

encountered in the ferrites, the tendency toward the maximum number of unpaired electrons is maintained, and a contribution of five unpaired spins per ion is expected; however, measurements of the magnetization of these compounds do not support this expectation.

To understand this discrepancy, it is necessary to examine the electronic energies of the ions in cubic fields. If both ions are to maintain five unpaired spins, the splitting diagram in Fig. 3 demands that two of the electrons have the higher cubic field energy values and three the lower. The total energy in this case turns out to be the same as if all five electrons had the free ion energy values. In other words, placing Fe^{3+} and Mn^{2+} into cubic crystalline fields does not raise or lower their electronic energies.

If, however, the Fe^{3+} and Mn^{2+} ions exchange valences, becoming Fe^{2+} and Mn^{3+} , the energy situation changes considerably. The Mn^{3+} ion in the cubic electric field has four magnetic electrons with unpaired spins. Three of these electrons will have the lower energy value. The fourth electron will have the higher value. Since there are now three electrons with low energies and only one with a high energy, Mn^{3+} will have a reduced electronic energy when transferred from free space into a cubic crystalline field. The Fe^{2+} ion has six magnetic electrons. To maintain the maximum number of unpaired spins and still have a low electronic energy, four electrons must have low energies and two the higher energy. Within the group of four low-energy electrons, two are required to be spin-paired, leaving only two unpaired spins. The two high-energy electrons will be unpaired so that the Fe^{2+} ion possesses a net moment of four unpaired spins. Because there are now four electrons with low energies and only two with the higher energy, Fe^{2+} also will have a reduced electronic energy when placed in cubic fields.

By lowering the electronic energies of Fe^{2+} and Mn^{3+} , the cubic field enhances the stability of these ions in crystals. It becomes reasonable to expect therefore, that Fe^{2+} and Mn^{3+} will be the coexisting ionic species in the ferrites rather than Fe^{3+} and Mn^{2+} . The fact that Fe^{2+} and Mn^{3+} carry only four unpaired spins is now sufficient to explain the magnetization measurements on these compounds. (An experimental verification of the coexistence of Fe^{2+} and Mn^{3+} in the magnetic oxides has recently been achieved by Dr. Arthur Miller, RCA Laboratories.¹)

In summary, this example illustrates the effect of the crystalline electric field in promoting the transfer of an electron

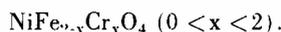
from one kind of ion to another. Electron transfers of this nature always alter the magnetism of the ions involved and most often also change the magnetic properties of materials containing these ions.

SPIN-QUENCHING MECHANISM

In recent years, a number of laboratories have prepared a variety of magnetic oxides containing significant amounts of chromium. In the oxides the stable ionic species is Cr^{3+} which has three magnetic electrons. It is usually assumed that the three electrons each contribute an unpaired spin to the magnetic moment. The saturation magnetization of most of these materials, however, has been found to be anomalously low.

In cubic crystalline fields, Cr^{3+} does indeed have three unpaired spins. Reference to Fig. 3 shows that the Cr^{3+} ion can maintain both a maximum number of unpaired spins and a minimum energy by requiring three electrons with unpaired spins to assume the lowest cubic field energy value. In those compounds where anomalously low magnetization values have been observed, the Cr^{3+} ions are found to reside in crystalline electric fields of tetragonal rather than cubic symmetry. To maintain the maximum number of unpaired spins in a tetragonal field, the energy diagram in Fig. 3 demands that two electrons have the lowest energy values and one the next highest. If the tetragonal field becomes very strong in these materials, the energy difference between the two lowest levels may become quite large. In that event it becomes energetically uneconomical to keep an unpaired electron with such a large energy. The tendency to maintain three unpaired spins is then overcome by the crystal field. The high-energy electron will assume the low-energy value by pairing its spin with one of those electrons already possessing the low energy. The total number of unpaired spins is thereby reduced from three to one.

The concept of the spin quenching of Cr^{3+} is particularly successful² in explaining the low magnetization of such magnetic materials as NiCr_2O_4 and CuCr_2O_4 . An especially illustrative example is the magnetization behavior of the compositional system



The observed saturation magnetization³ of this system as a function of the compositional parameter x is shown in Fig. 4. Curve A is the theoretical prediction of this behavior based on the assumption that Cr^{3+} has three unpaired spins. Curve B represents the prediction of the crystal field point of view based on the conclusion that Cr^{3+} is spin quenched

with a single unpaired spin. A comparison of these curves makes it clear that the application of the crystal field theory has provided a considerable improvement in our knowledge of the magnetic behavior of these materials.

SUMMARY

There are also many properties of the magnetic oxides besides magnetization which are just as strongly influenced by the internal crystal fields. Some of the more important of these include the magnetic anisotropy, the magnetostriction, the distribution of the magnetic ions in the crystal lattice^{4,5}, and the cooperative deformations of the crystal lattice.⁶

The explicit use of the crystal-field point of view in magnetic materials research has been initiated only within the past few years. Further developments of the crystal field theory itself and of its application to the important areas of magnetic behavior are now being pursued in laboratories throughout the world.

REFERENCES

1. Miller, A., "Resolution of the Ambiguity of Valence States in Spinel Containing Manganese and Iron," *Phys. Rev.*, in press.
2. Baltzer, P. K., Wojtowicz, P. J., "On the Origin of Low Moments in Chromium-Containing Spinel," *J. Appl. Phys.* Vol. 30, supplement, April 1959.
3. McGuire, T. R. and Greenwald, S. W., private communication.
4. McClure, D. S., "The Distribution of Transition Metal Cations in Spinel," *J. Phys. Chem. Solids*, Vol. 3, 1957.
5. Miller, A., "Distribution of Cations in Spinel," *J. Appl. Phys.*, Vol. 30, supplement, April 1959.
6. Wojtowicz, P. J., "Theoretical Model for Cubic-to-Tetragonal Phase Transformations in Transition Metal Spinel," *J. Appl. Phys.*, Vol. 30, supplement, April 1959 and *Phys. Rev.*, in press.

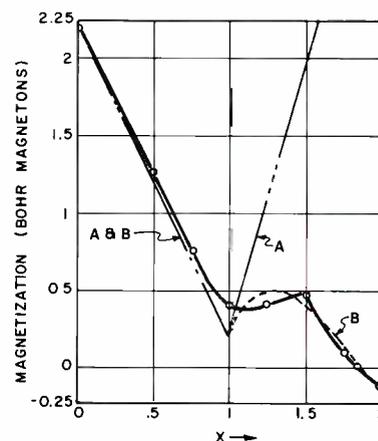


Fig. 4—Magnetization vs. composition in the system, $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ (Experimental points after McGuire and Greenwald).

NEW FERRITES FOR ELECTRONICS

by

H. LESSOFF, Dr. W. J. CROFT, and J. H. McCUSKER

*Advanced Development
Semiconductor and Materials Division
Needham Heights, Massachusetts*

NICKEL-ZINC FERRITES have been widely used in intermediate-frequency transformers, wide-band transformers, and miniature inductors because of their linear B-H characteristics, low induction levels, and high stability. The improvement of other properties of these materials is desirable, however, in such areas as higher frequency range, temperature stability, mechanical shock resistance, higher saturation induction, and lower losses at moderate induction levels.^{1,2} This paper describes improvements obtained in frequency characteristics, magnetic quality factor (Q), and temperature stability.

PREPARATION AND MEASUREMENTS

Nickel-zinc ferrites are magnetically soft ceramics prepared from oxides of iron, nickel, and zinc. Like magnetite, the ferrites have spinel-type structure. Their resistivity is higher than that of magnetite because all of the iron is in a higher state of oxidation and, therefore, eddy-current losses are low.

Ferrites are processed by the standard ceramic technique of blending the oxides, adding a binder, pressing, and firing. The electrical properties of the finished component can be varied by varying such processing conditions as firing temperatures and pressing pressures. The addition of trace amounts

of certain impurities to the ferrite also affects electrical and magnetic properties. The effects of many additives under different firing conditions were studied to determine the resulting properties of the final ferrite body. Of the additives investigated, the following proved beneficial: molybdenum oxide, barium oxide, cobalt oxide, and carbon black. The properties influenced were high-frequency response of initial permeability (μ'), the magnetic quality factor (Q), and the temperature coefficient of initial permeability (TC).

Electrical properties of the components were measured with Boonton type 190A and 260A Q-meters, a 60-cycle hysteresis-loop tester, and a slotted-line. The initial permeability for frequencies below 50 megacycles was calculated from the following equation:

$$\mu' = \frac{L_i}{L_o}$$

where L_i is the measured inductance of the sample and L_o is given by the following expression:

$$L_o = 1.17 \times 10^{-2} N^2 H \log_{10} \frac{d_1}{d_2}$$

where N is the number of turns in the

toroid, H is the height in inches, and d_1 and d_2 are the outside and inside diameters, respectively.

Above 50 megacycles, measurements were made with a coaxial sample holder on both a Q-meter and on slotted-line apparatus. Good agreement was observed with both.

ADDITIVE EFFECTS

The temperature coefficient of initial permeability (TC) of a nickel-zinc ferrite was varied by controlled addition of fine-particle carbon black. The smaller the particle size of the carbon added, the lower the TC became. The smallest size available, 100-angstrom material, gave the best results. Within a given particle range, the amount of carbon black added also controlled the temperature coefficient. Increasing the amount of carbon black tended to lower the TC and, in fact, it was possible to make the temperature coefficient negative. The RCA Micro-module now uses ferrite toroids stabilized with carbon black for 4.3-megacycle inductive elements.

Barium additions to ferrites increase the maximum operating frequency and lower the TC . Barium ferrite,^{3,4} which is magnetically hard, has a hexagonal crystal structure and is widely used in permanent magnets. The mixture of cubic, magnetically

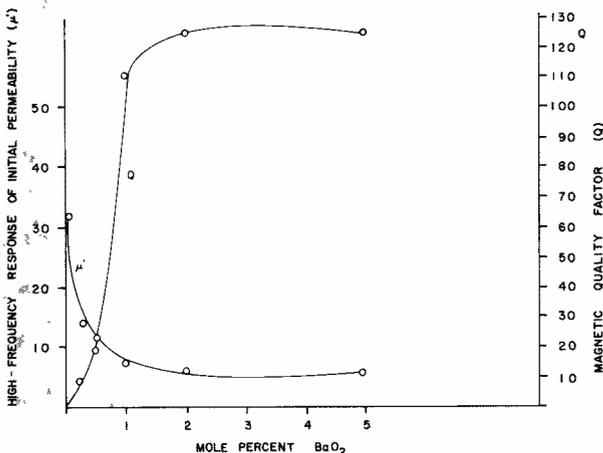


Fig. 1—Effect of barium oxide additions on high-frequency response of initial permeability (μ') and magnetic quality factor (Q) at 100 megacycles.

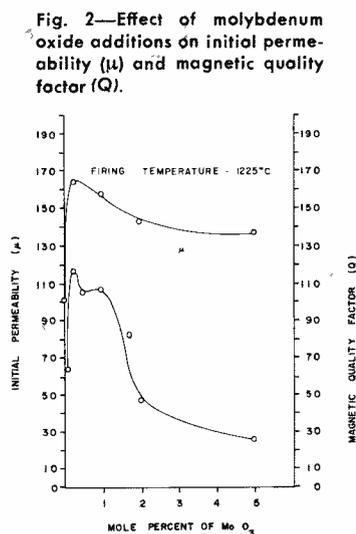


Fig. 2—Effect of molybdenum oxide additions on initial permeability (μ) and magnetic quality factor (Q).

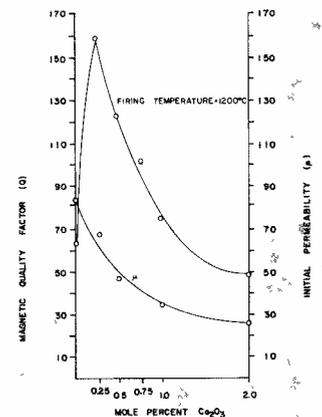


Fig. 4—Effect of cobalt-oxide additions on initial permeability (μ) and magnetic quality factor (Q).

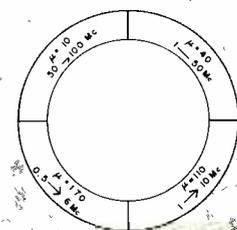


Fig. 3—Multicomponent ferrite toroid.

soft ferrites with magnetically hard barium ferrite^{4,5} provides a class of ferrites having fairly constant permeability up to approximately 1000 megacycles. The addition of barium oxide to nickel-zinc ferrite results in a large decrease in μ' , but the Q is higher over a greater frequency range.

The effect of additions of barium oxide on initial permeability and quality at 100 megacycles is shown in Fig. 1. The useful frequency range of a ferrite containing 5-mole-percent barium oxide is from 10 to 130 megacycles. The temperature coefficient of initial permeability is also affected by barium additions; with a 5-mole-percent addition, the TC is 0 ± 100 parts per million per degree centigrade. This type of material is also being used in the RCA Micromodule equipment at 50 megacycles.

Small additions of vanadium oxide,^{6,7,8} arsenic oxide,^{9,10} and copper oxide^{9,10} to magnetically soft ferrites increase the initial permeability and lower the coercive force, but reduce the quality factor Q . These impurities probably act as fluxing agents during firing.

Small additions of molybdenum oxide increase both initial permeability and Q in nickel-zinc ferrites, as shown in Fig. 2, but additions of greater than 1.0-mole-percent molybdenum oxide result in a decrease in both initial permeability and the quality factor. The combination of molybdenum and barium or cobalt oxides

TABLE I—PROPERTIES OF TYPICAL FERRITES WITH SMALL ADDITIONS OF OXIDES OF Mo, AND Ba OR Co.

| Frequency (megacycles) | μ' | Q | $\mu Q \times 10^{-3}$ |
|---------------------------|--------|-----|------------------------|
| 0.5 | 170 | 290 | 49 |
| 4.0 | 175 | 115 | 22 |
| 11 | 110 | 130 | 14 |
| 25 | 70 | 150 | 10 |
| 50 | 10 | 110 | 1.1 |
| 200 | 10 | 110 | 1.1 |
| 200 | 15 | 80 | 1.2 |
| 300 | 11 | 75 | 0.83 |
| 300 | 6 | 110 | 0.66 |
| 500 | 10 | 40 | 0.4 |
| 500 | 7 | 80 | 0.56 |
| 1000 | 10 | 4 | 0.04 |

results in ferrites useful for inductor material in the frequency range of 0.5 to 500 megacycles. The properties of some typical ferrites resulting from small additions are shown in Table I. At several hundred megacycles, the μQ product is about 100. Combination of various ferrites in a single toroid, as shown in Fig. 3, permits the variation of frequency response or inductance in a single ferrite body.

The effect of small cobalt additions to ferrites has been investigated by Van der Burgt¹¹, Van Uitert¹², and Bradley,^{13,14} among others. Cobalt has a large effect on the magnetic crystalline anisotropy of a ferrite, and changes the magnetic properties of nickel-zinc ferrite. Resistivity increases, Q increases, and initial permeability decreases. Fig. 4 shows the effect of cobalt additions to a nickel-

zinc ferrite. Most commercial inductor ferrites have small amounts of cobalt in the ferrite formulation.

SUMMARY

By controlled additions of various oxides, inductor materials can be prepared for wide frequency applications. New inductive elements for use in the FM and TV frequency ranges now appear practical. Some degree of control of the temperature characteristics of inductive elements is possible for use in temperature-compensated tuned circuitry.

BIBLIOGRAPHY

1. C. D. Owens, *Trans. I.R.E. on Component Parts, CP-3*, 54 (1956).
2. C. D. Owens, *Proc. I.R.E.*, **44**, 1234 (1956).
3. H. Fahlenbrach and W. Heistes: *Arch. Eisen. Littena.* **24**, 523 (1953).
4. J. J. Went, G. W. Rattrenau, E. W. Gorter, and G. W. vanOosterhout, *Philips Tech. Rev.* **13**, 194 (1952).
5. G. H. Jonker, H. P. J. Wijn, and F. B. Braun: *Philips Tech. Rev.* **18**, 145 (1956).
6. L. T. Piekarski, U. S. 2,744,873 (May 8, 1956).
7. L. C. F. Blackman, *J. Appl. Phys.* **28**, 1511 (1957).
8. D. M. Grimes, et. al., *J. Appl. Phys.* **26**, 2205 (1955).
9. Mitsuo Sugimoto, et. al., *Repts. Sci. Research Inst. (Japan)* **32**, 61 (1956).
10. L. G. Van Uitert, *J. Appl. Phys.* **27**, 723 (1956).
11. C. M. Van der Burgt, *Philips Res. Rep.* **12**, 97 (1957).
12. L. G. VanUitert, *J. Chem. Phys.* **24**, 306 (1956).
13. F. Bradley, *Ceramic Age*, **31**, (Sept. 1958).
14. F. Bradley, *Ceramic Age*, **33** (Nov. 1958).



J. H. McCUSKER received his B.S.E.E. from Northeastern University in 1947 and the M.S.E.E. from M. I. T. in 1949. From 1944 to 1946, he served as an engineer for the U. S. Atomic Energy Project, developing high-vacuum physical techniques associated with mass spectrometers, ionization chambers, and isotope determinations. In 1949 he became an instructor in Electrical Engineering at Pennsylvania State Uni-



HOWARD LESSOFF received his B.S. in 1953 and his M.S. in 1957, both in chemistry from Northeastern University. He was a chemist with the Quartermaster Corps working on petroleum quality control, from 1953 to 1955. From 1955 to 1956, he was with the Retina Foundation in biochemical research, and from 1956 to 1957 was a Research and Teaching Associate at Northeastern University, where he did fluorocarbon research. Since 1956 he has taught in the Lincoln



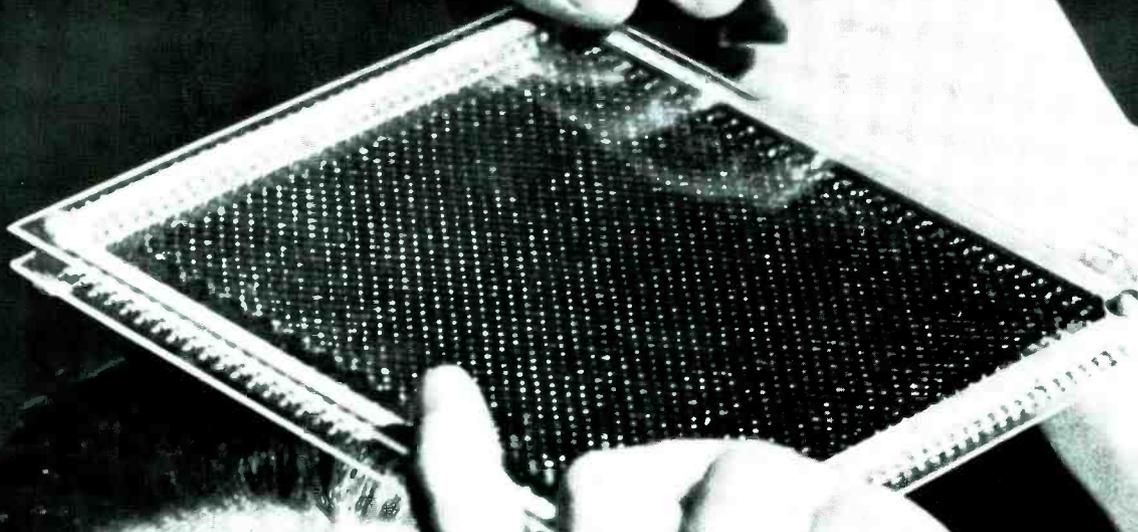
DR. WILLIAM J. CROFT received the B.S. in 1950, and the M.A. in 1952, in mineralogy, and his Ph.D. in crystallography and mineralogy in 1954, all from Columbia University. He taught at Hofstra College for one year, and in 1955 joined the staff of M. I. T.'s Lincoln Laboratory to engage in crystallographic studies of magnetic materials. He joined the

versity. He returned to M. I. T. in 1951 as Chief of the Materials Evaluation Section for the Computer Division, M. I. T. Lincoln Laboratory. Mr. McCusker joined the Components Division of RCA in May of 1956, and has since devoted his time to the establishment of the electrical measurement laboratory for Materials Advanced Development Laboratory at Needham. He is presently manager of Advanced Development.

Institute at Northeastern. He joined the RCA SC & M Division at Needham in 1957, working on ceramic and tantalum capacitors, thin films, and low-loss high-resistance ferrites, as well as synthesizing mixed oxides for thermo-electric power generation. He has several patent applications on low-loss ferrites, and a publication. He is a member of the American Chemical Society and the Electrochemical Society.

RCA SC & M Division, Needham, in April 1957, and has since been involved in crystallographic studies of ferrites and semi-conducting compounds. He is a member of the Mineralogical Society of America, The Mineralogical Society of England, The American Crystallographic Association, and the Society of the Sigma Xi.

DEVELOPMENT OF SQUARE-LOOP FERRITE MEMORY CORES



DEFINITION OF TERMS

1. **Driving current (I_m):** the peak value of the current pulse required to switch a core from its 1 state to its zero state, or vice versa.
2. **Switching time (t_s):** the time interval between the instant the driving current rises to 10 percent of its peak value and the instant the *undisturbed 1* (uV_1) decays to 10 percent of its peak value.
3. **Undisturbed 1 response voltage (uV_1):** the peak value of the output voltage produced when a core is switched from its *undisturbed 1* state to its zero state by a current pulse having an amplitude equal to the driving current I_m .
4. **Disturbed zero response voltage (dV_2):** the peak value of the output voltage produced when a core which is in its *disturbed zero* state is subjected to a *read* pulse having an amplitude equal to the driving current I_m .
5. **Peaking time (t_p):** the time interval between the instant the driving current rises to 10 percent of its peak value and the instant the uV_1 reaches its peak value.
6. **Break current (I_b):** the maximum partial-write current ($I_{p,w}$) at a given driving current (I_m) which a core in the zero state will tolerate without any substantial increase or change in the amplitude of the *disturbed zero*.
7. **Current-pulse rise time (t_r):** the time interval between the instant the driving current rises to 10 percent of its peak value and the instant it rises to 90 percent of its peak value.
8. **Current-pulse duration (t_d):** the time interval between the instant the driving current rises to 50 percent of its peak value and the instant at which it falls off to 50 percent of its peak value.

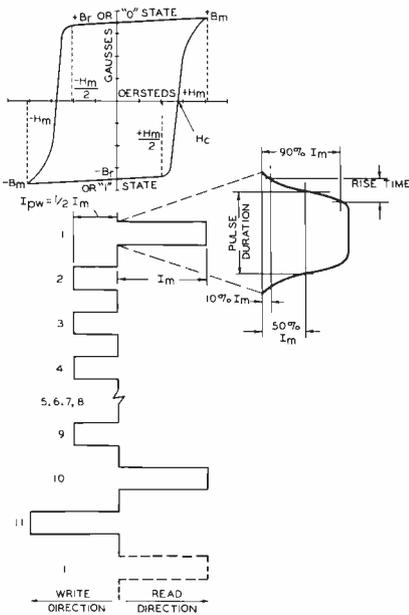


Fig. 1—Hysteresis loop and pulse program sequence.

This paper discusses the operating principles of magnetic cores in the coincident-current memory application, defines the core properties of interest and illustrates them by data on typical cores, and gives two examples of the application of the fundamental understanding of materials: (1) to develop an improved version of an existing core by the use of a different material and (2) to develop a faster core, using the same material.

OPERATING PRINCIPLES

The operation of a ferrite core in coincident-current memory application is explained in terms of the hysteresis loop shown in Fig. 1. The $-B_r$ state of the core is defined as the binary digit 1 and the $+B_r$ state as 0. If a current pulse producing a magnetizing force $+H_m$ (read) is applied to a core in its $-B_r$ state, the core switches to the $+B_r$ state, and a large signal voltage (uV_r) is induced in a wire passing through the core. If a second current pulse producing a magnetizing force $+H_m$ is then applied to the core, the flux changes only slightly, and the induced voltage signal is small. The state produced by this current pulse is called the undisturbed zero state.

A ferrite core for coincident-current application must have good signal-to-noise ratio when read. In addition, its magnetic properties must be such that the flux will not change significantly when magnetizing forces up to one half that required to switch the core

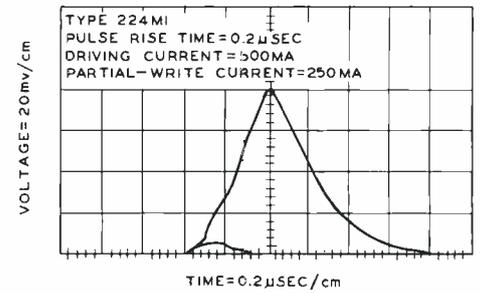


Fig. 4—Response voltage of XF-3018H.

(i.e., $-H_m/2$ or $+H_m/2$) are applied. Thus, if a series of current pulses each producing a magnetizing force $-H_m/2$ is applied to a core in its $+B_r$ or 0 state, the first few pulses of the series should cause only slight degradation of the zero state, and the remaining pulses should produce no further change. The state produced by the first few pulses is called the disturbed zero state.

The pulse program shown in the lower part of Fig. 1 is employed in the testing of memory cores and was used to generate the data given in Figs. 2 through 10. It produces the following sequence of events: Pulse No. 1 reads an undisturbed 1 output signal (uV_r) which was written by pulse No. 11 of the previous cycle. When pulse No. 1 is completed, the core is left in its undisturbed zero state. Pulses No. 2 through 9 are partial write pulses which only degrade the flux slightly to its disturbed zero state as long as the core is square and not overdriven.

J. J. Sacco, right, and L. B. Smith, left. (See inside front cover.)

JOSEPH J. SACCO, JR., received the B.S. degree in Chemistry from Northeastern University in 1952. He joined the Chemistry Section of the Computer Division of the MIT Lincoln Laboratories the same year and worked on the development of memory-core ferrites. He later became Leader of the Pilot Plant, and remained at the Laboratories until 1956. Since that time, he has been Manager of Magnetic Product Development of the Semiconductor and Materials Division at Needham, Mass.

by

J. J. SACCO, JR., Mgr.

Magnetic Product Development
Semiconductor and Materials Division
Needham Heights, Massachusetts

THE DEVELOPMENT OF the magnetic-core memory has made possible a marked increase in the speed, reliability, and memory capacity of digital computers. The rapid and extensive application of magnetic storage techniques has been made possible only by the availability in large quantities of high-quality memory cores. The development of memory cores, and of methods for mass production of uniform cores, has been so successful that cores can now be designed for specific applications and manufactured in large quantities to rigid specifications.

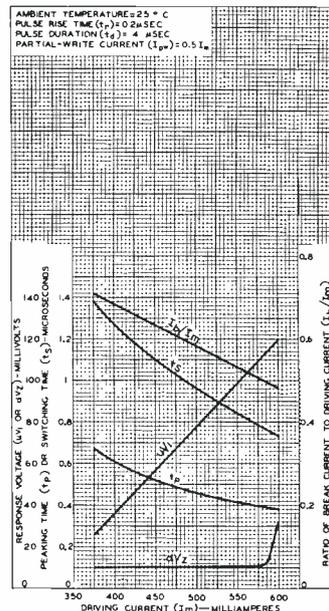


Fig. 2—Average characteristics of XF-3018H.

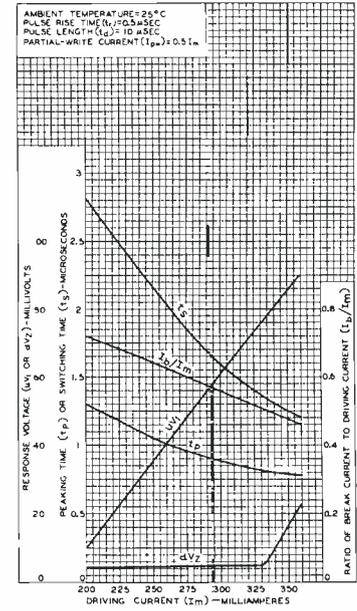


Fig. 3—Average characteristics of XF-3673.

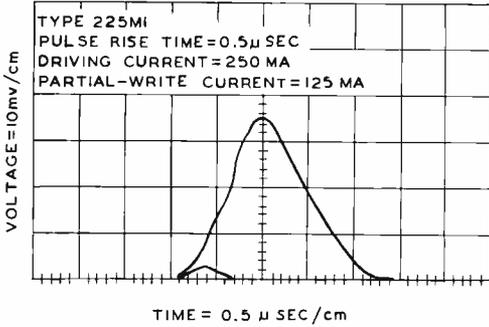


Fig. 5—Response voltage of XF-3673.

Pulse No. 10 reads the disturbed zero output signal (dV_z) and returns the core to the undisturbed zero state. Pulse No. 11 then switches the core to the undisturbed 1 state.

TYPICAL CORE PROPERTIES

The most important parameters involved in the fabrication and selection of a ferrite core are its driving-current requirements (I_m) and switching time (t_s). Other factors are the undisturbed 1 response voltage (uV_1), disturbed zero response voltage (dV_z), peaking time (t_p), and break current (I_b). Both the voltage outputs and switching times are affected by the amplitude and shape of the current pulses. The pulse shape is normally defined in terms of rise time (t_r), duration (t_d), and overshoot for a given amplitude (See *Definition of Terms* for an explanation of these and other parameters.)

Types XF-3018H and XF-3673 are typical production cores having the same dimensions (0.050-inch outer diameter, 0.030-inch inner diameter) but different current and switching characteristics. Type XF-3018H, which has a switching time of approximately 1 microsecond at a nominal driving current of 500 milliamperes, is used primarily in computers which require a relatively fast cycle time. Type XF-3673, which has a switching time of about 2.2 microseconds at a nominal driving current of 250 milliamperes, is used mainly in commercial applications which require a lower driving current.

Figs. 2 and 3 show the average

characteristics of XF-3018H and XF-3673 cores when the pulse program shown in Fig. 1 is used and the current amplitude is varied. The data for the various parameters were compiled from hundreds of acceptable cores representing different production batches and firing conditions. This information was then averaged and plotted as a function of driving current at 2-to-1 coincidence. Individual values of t_s , t_p , and dV_z vary only slightly from the average values, while the variation in uV_1 and I_b for a given firing condition and between different firing conditions is generally about ± 10 percent around the average figures. Figs. 4 and 5 represent the response voltage of the two cores as displayed on an oscilloscope. The large trace shows uV_1 and the small trace dV_z .

Coercive force (H_c), threshold field (H_o), and the switching coefficient (S_w) are more-fundamental parameters which can be related to the driving-current requirements (I_m) and switching characteristics (t_s). The coercive force (H_c) is defined as the applied field for a major hysteresis loop at which the induction (B) is zero. The switching coefficient, S_w , is the reciprocal slope of the linear region of the plot of the reciprocal switching time ($1/t_s$) versus the applied field (H). The intercept on the H axis of the extrapolation of the linear portion of the S_w plot is known as the threshold field (H_o), which is the field required to maintain motion of a

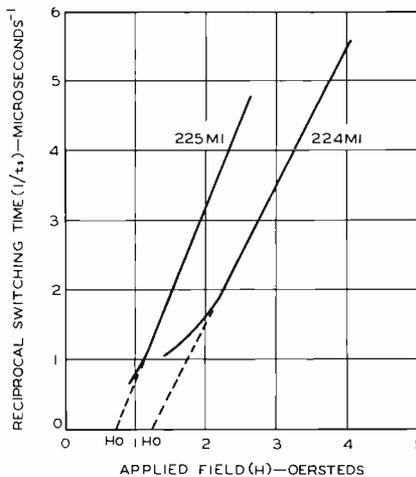


Fig. 6—Switching constant curves (S_w) for XF-3018H and XF-3673.

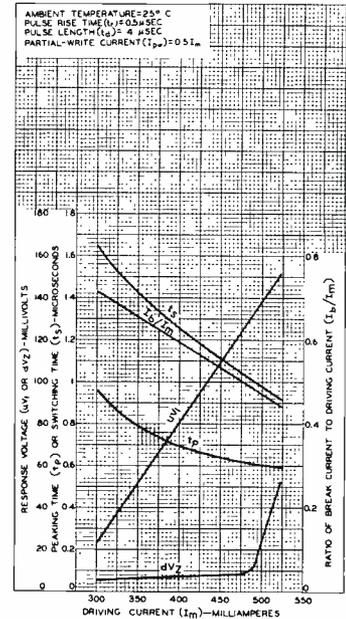


Fig. 7—Average characteristics of XF-4028.

domain wall. These parameters are related by the following equation, where H_o is approximately equal to H_c .

$$S_w = (H - H_o) t_s$$

This equation applies only when all the flux is being switched and only for one type of domain switching. In this region, H is usually much greater than H_o , and the equation can be written to a first approximation as $S_w = H t_s$. This equation, which would apply to cores used as switches, indicates that lower S_w materials are preferable for a given H . The S_w equation does not apply rigidly in the 2-to-1 coincident-current region because not all the flux may be switching, but it does indicate inherent switching properties of the material. In the coincident-current region, $H = H_m \cong 2H_c$, or $2H_o$. Thus, S_w in this region for qualitative considerations can be written as $S_w = H_c t_s$.

Fig. 6 shows the S_w plot for two memory cores, types XF-3018H and XF-3673. The value of S_w is 0.5 oersted-microsecond for type XF-3018H and 0.4 oersted-microsecond for type XF-3673. Because the S_w 's of both cores are about the same, while the coercive force of the XF-3673 core is about 0.6 oersted as compared to 1.2 oersteds for the XF-3018H core, the switching time for type XF-3673 in current coincidence should be and is about twice that of type XF-3018H.

DEVELOPMENT OF IMPROVED CORES
Decreased Current. If the S_w is lower,

cores having improved properties should be possible. Because the S_{ic} for the XF-3673 core is 20 percent lower (or faster) than that of the XF-3018H core, it was thought that the XF-3673 material could be used and its normal coercive force increased by means of firing-temperature changes. A substitute for the XF-3018H core could then be made with either a 20-percent reduction in switching time at the same driving current, or the same switching time with a 20-percent reduction in driving current. It was decided that the reduction in driving current was most desirable.

As stated previously, the coercive force (H_c) of the XF-3018H core is approximately 1.2 oersteds. If the XF-3673 material is to be processed to obtain the same switching time as that of type XF-3018H, therefore, its coercive force would have to be approximately 0.96 oersted—a reduction of 20 percent from the coercive force of the XF-3018H core. This result can be shown by the following reasoning:

$$S_{ic} (\text{XF-3018H}) = 0.5 = \frac{H_c (\text{XF-3018H}) t_s}{t_s}$$

$$S_{ic} (\text{XF-3673}) = 0.4 = \frac{H_c (\text{XF-3673}) t_s}{t_s}$$

Thus, for the same switching time

$$(t_s) H_c (\text{XF-3673}) = H_c (\text{XF-3018H}) (0.4/0.5) = 0.8 (1.2) = 0.96$$

The proper firing-condition changes were determined, and the resulting core was designated type XF-4028. Its average characteristics and response voltage are shown in Figs. 7 and 8. The nominal driving current for the XF-3018H core is 500 milliamperes, while

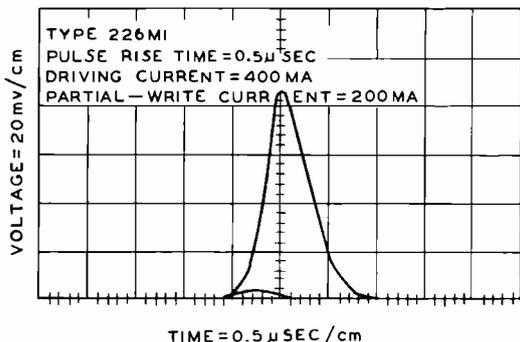


Fig. 8—Response voltage of XF-4028.

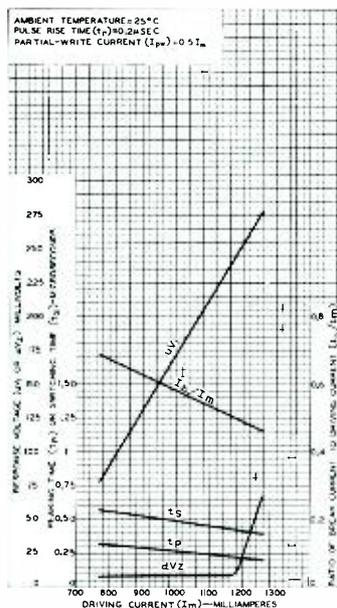


Fig. 9—Average characteristics of XF-4046.

that of the XF-4028 core is 400 milliamperes. In the case of the XF-3018H core, the measurements were made with a 0.2-microsecond current rise time, while for the XF-4028 core, a 0.5-microsecond rise time was used. Because the switching time and peaking time of the XF-4028 core are longer because of the longer rise time, corrections for a 0.2-microsecond rise time lead to the following comparison:

| | XF-4028 | XF-3018H |
|--|---------|----------|
| Driving Current (I_m), ma | 400 | 500 |
| Switching Time (t_s), μsec (approx.) | 1 | 1 |
| Peaking Time (t_p), μsec (approx.) | 0.45 | 0.45 |
| Undisturbed 1 (μV_1) | | |
| Response Voltage, mv | 85 | 85 |
| Coercive Force (H_c), oersteds | 0.95 | 1.2 |

Faster Cores. Speeds faster than one microsecond in current coincidence were also required. This requirement led to the development of cores having switching times of a half microsecond or less. As stated previously, the coercive force at maximum squareness for the XF-3018H core is 1.2 oersteds, and the switching time for this coercive force is 1 microsecond. Because S_{ic} is a constant for a given composition, the following reasoning applies:

$$S_{ic} = H_c (\text{XF-3018H}) t_s (\text{XF-3018H}) = (H_{c_x}) t_{s_x}$$

$$(1.2) (1) = (H_{c_x}) (0.5)$$

$$H_{c_x} = 2.4 \text{ oersteds}$$

Therefore, to make a core having a 0.5-microsecond switching time using XF-3018H material, it is necessary to increase the coercive force from 1.2 to 2.4 oersteds. The necessary firing-condition changes were made, and the result was the memory core XF-4046. The average characteristics and response voltage of this core are shown in Figs. 9 and 10.

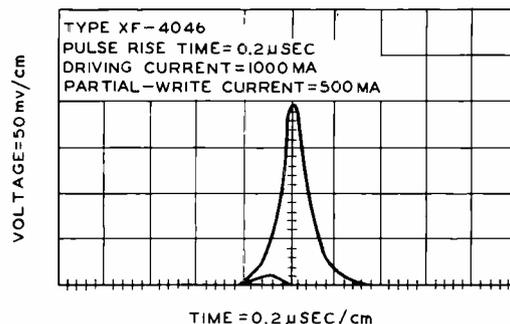
At nominal driving currents (0.2-microsecond rise time), the following comparison can be made:

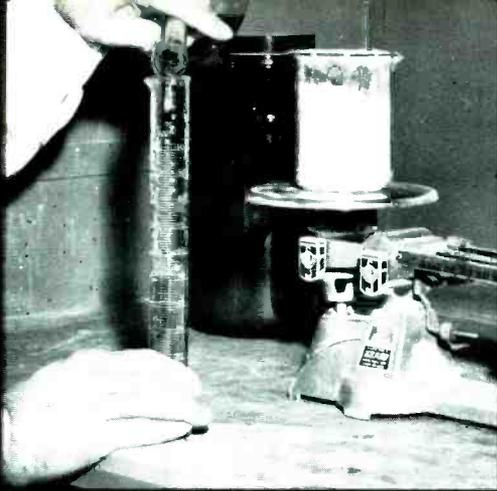
| | XF-4046 | XF-3018H |
|--|---------|----------|
| Driving Current (I_m), ma | 1000 | 500 |
| Switching Time (t_s), μsec (approx.) | 0.5 | 1 |
| Peaking Time (t_p), μsec (approx.) | 0.25 | 0.45 |
| Undisturbed 1 (μV_1) | | |
| Response Voltage, mv | 170 | 80 |
| Coercive Force (H_c), oersteds | 2.4 | 1.2 |

Therefore, by the use of the information from a few basic measurements, an existing material in the first case was converted into an improved version of a standard core of different composition. In the second example, the properties of a standard core were altered to fit a specific application.

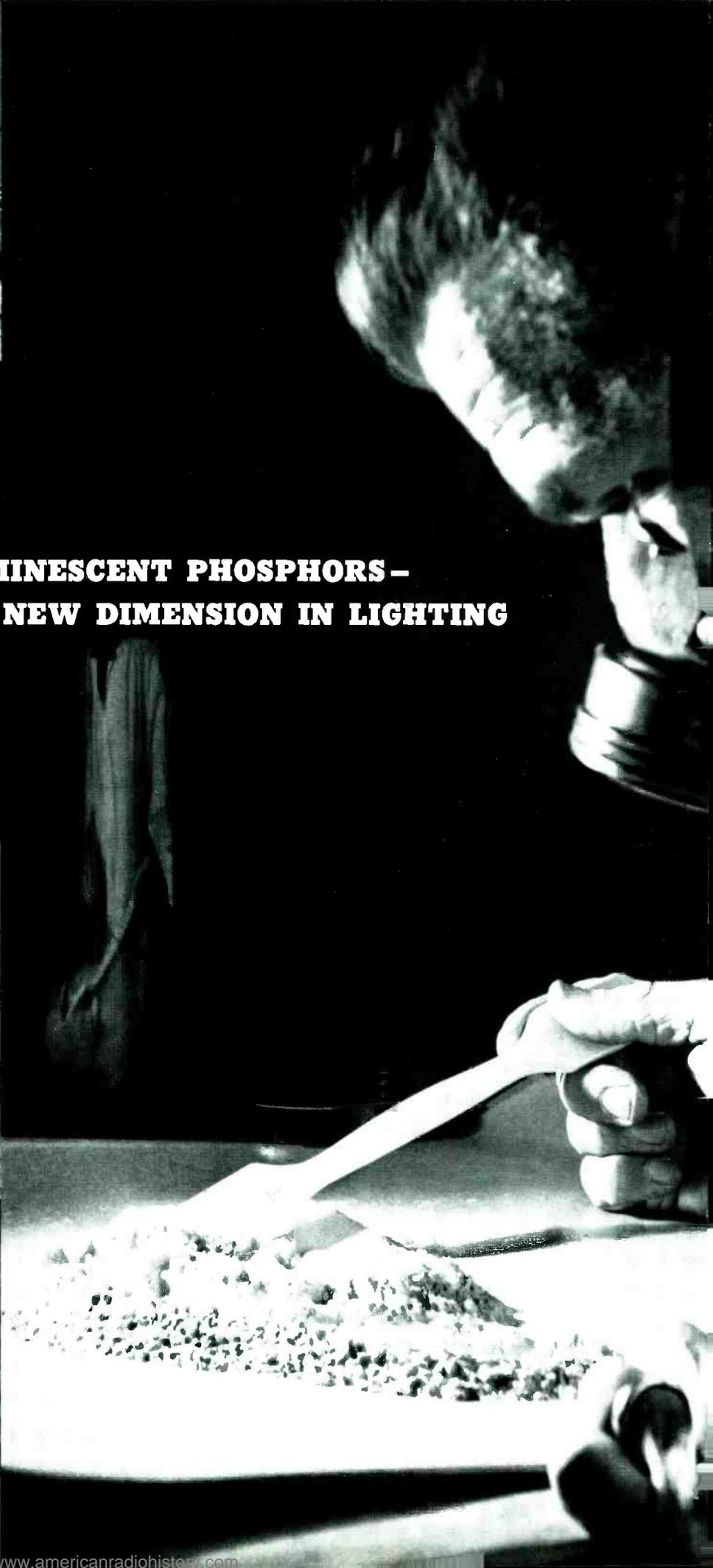
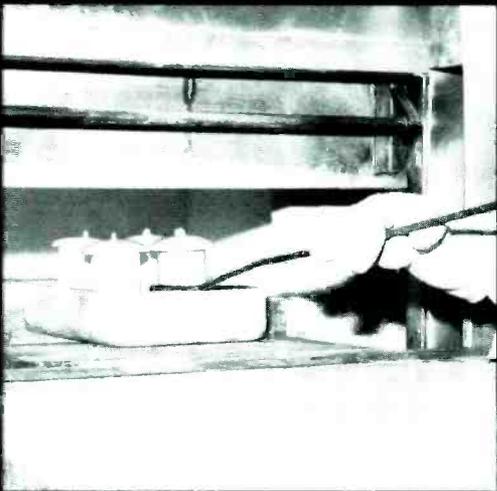
The possibility of further improvement and variations in existing cores is limited only by the fundamental parameter of S_{ic} and the permissible extent to which H_c can be varied. Materials having even lower values of switching constant ($S_{ic} = 0.3$) and coercive force ($H_c = 0.03$) have been or are now being developed.

Fig. 10—Response voltage of XF-4046.





**ELECTROLUMINESCENT PHOSPHORS –
GATEWAY TO A NEW DIMENSION IN LIGHTING**





by

J. P. STANAVAGE

*Chemical and Physical Laboratory
Electron Tube Division
Lancaster, Pennsylvania*

THE MOST EXCITING recent development in the field of lighting is electroluminescence. Light has previously been obtained from phosphors in such devices as fluorescent lamps and cathode-ray tubes. In fluorescent lamps, the phosphor is excited by radiation created when mercury is subjected to an electrical discharge; in cathode-ray tubes, the phosphors are excited by a stream of electrons from the cathode. In electroluminescence, however, the mode of excitation is an electric field.

A simple device utilizing electroluminescent (EL) phosphors is shown in Fig. 1. When a field is applied to the electrodes, the phosphor-dielectric layer, acting as a simple capacitor, emits light. Appropriate selection of substrate and electrodes permits light to be emitted from either or both sides of the layer.

The theoretical mechanism of electroluminescence has been covered in the literature. Most authors¹⁻⁹ consider the mechanism to be analogous with that for cathodoluminescence. However, recent developments at the David Sarnoff Research Center at Princeton indicate that the present theories may have to be revised. This paper describes the chemical nature of electroluminescent phosphors and their electronic characteristics (i.e., spectral emission, brightness, efficiency, and life), and compares electroluminescence with other light sources.

PREPARATION OF PHOSPHORS

The number of host materials which can be used for practical electroluminescent phosphors is extremely limited in comparison with those available for phosphors excited by other means. In

the field of cathodoluminescence, the halide, phosphate, silicate, sulfide, selenide, and other salts of elements in Groups I and II of the periodic chart offer almost unlimited possibilities as base materials. In the field of electroluminescence, however, the only practical host materials found to date have been zinc sulfide, zinc selenide, and their solid solutions.

Similarly, there is a shortage of suitable activators and coactivators, or "charge compensators," for use in this field. In the field of cathodoluminescence, silver, copper, and manganese are the most common activators, but many of the "transition" or rare-earth elements can also be used as activators or intensifiers. In electroluminescence, however, the activators available are even more limited than the host crystals. Although manganese is used in some cases, the only practical activator is copper. These limitations naturally restrict the electronic and applications properties of the phosphors.

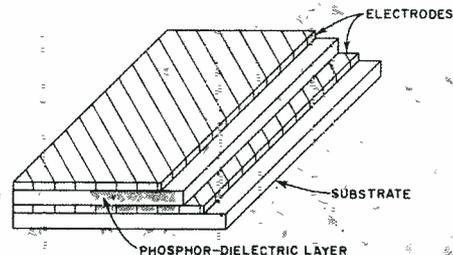
Even with this limited phosphor system, however, materials having spectral emission covering the visible region can be prepared by careful control of preparative conditions, such as firing temperature, flux, activator concentration, coactivator, and atmosphere during firing. At present, deep blue, green, green-yellow, deep yellow, red, and white emitters can be obtained by strict process control. Fig. 2 shows normalized spectral response curves of phosphors prepared from zinc sulfide, selenide, and their solid solutions using various coactivators.

PHOSPHOR CHARACTERISTICS

To date, five electroluminescent phosphors have been standardized, ranging in color from a deep blue emitting at about 4550 angstroms to a deep yellow emitting at about 5850 angstroms and a white. The spectral-emission curves for these phosphors

Fig. 1—A simple device utilizing EL phosphors.

Technician L. B. Denlinger inspects an electroluminescent phosphor under ultraviolet light for impurities. Top left: Compounding a formulation for an EL phosphor. Left center: Removing a sample phosphor from an electric furnace after reaction. Bottom left: Measuring brightness of an EL phosphor.



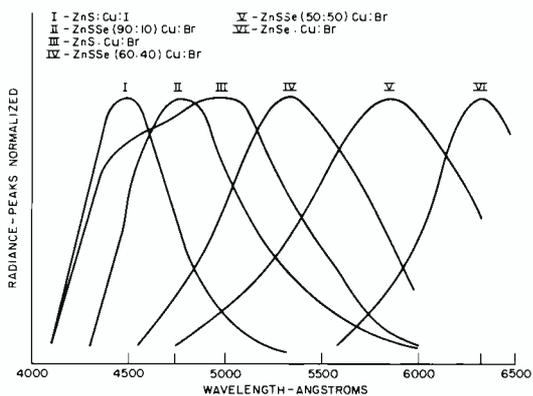


Fig. 2—Effect of composition on spectral emission.

are shown in Fig. 3. The brightest phosphors are those which emit near the peak of the eye-sensitivity curve (5550 angstroms). The spectral emission is independent of voltage, but is a function of operating frequency. An increase in frequency shifts the spectral response towards the ultraviolet region. Maximum shift can be as high as 300 angstroms. Fig. 4 illustrates the frequency dependency of some typical electroluminescent phosphors.

The effect of voltage and frequency on brightness is shown in Figs. 5 through 9. Brightness generally increases linearly with frequency up to approximately 2000 cycles per second. Under normal operating conditions, brightness varies with the third power of the voltage. The voltage-response curve can be controlled within the range of about V^{1-4} by careful selection of operating conditions and application techniques. As the voltage per unit thickness of phosphor layer is increased, the voltage response becomes more linear with respect to brightness. At constant voltage, it is

obvious that phosphor-layer thickness is a controlling factor of brightness. More-nearly linear voltage-response curves are obtained when the phosphor is imbedded in a ceramic dielectric than when plastic is used. Prolonged operation generally increases the slope of the voltage-response curve.

EFFICIENCY AND LIFE

The efficiency of electroluminescent phosphors (lumens per watt), like the brightness, is highest for those which emit near the peak of the eye sensitivity curve. The efficiency of most electroluminescent phosphors reaches a maximum when they are operated in the frequency range from 400 to 1000 cycles per second and the voltage range from 100 to 150 volts per mil. The dielectric in which the phosphor is imbedded can also affect the efficiency. Phosphors imbedded in some plastics can be twice as efficient as those imbedded in glass.

Phosphor treatment after firing is critical and can change the efficiency

by an order of magnitude. The operating efficiency of electroluminescent panels prepared from the phosphors discussed above ranges from 4 to 8 lumens per watt. These values compare with efficiencies of 15 to 75 lumens per watt for incandescent and fluorescent bulbs, respectively. Efficiencies of a much higher magnitude can be obtained if the panels are operated at optimum frequency and voltage and corrections are introduced for the light absorbed by the transparent electrodes and the dielectric, for edge emission, for emission from both sides of a panel, and for other similar factors. Unfortunately, although these corrections increase the magnitude of the efficiency, they do not improve the operating characteristics. Operating life has little effect on efficiency. Although brightness decreases on life, the power consumption also decreases; consequently, the efficiency remains constant.

One of the major problems encountered with electroluminescent panels is the decrease in brightness during operation. Typical life curves are shown in Fig. 10. The deterioration on life is caused partly by the physical make-up of the phosphor and the dielectric. The effects of chemical composition and charge compensator were mentioned previously. Environment and operating conditions also affect the rate of brightness deterioration. Continuous exposure to high humidity is extremely deleterious. The rate of brightness loss is approximately a function of the square of humidity difference (i.e., life is four times better at a relative humidity of 25 percent than of 50 percent). As

Fig. 3—Typical spectral-energy emission characteristics of EL phosphors.

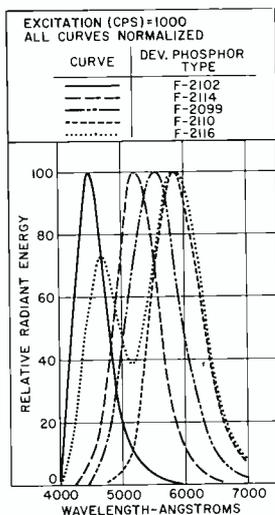


Fig. 4—Effect of frequency upon spectral emission.

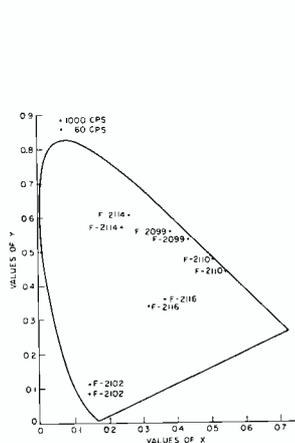


Fig. 5—Typical brightness characteristics of blue EL phosphors (F-2102).

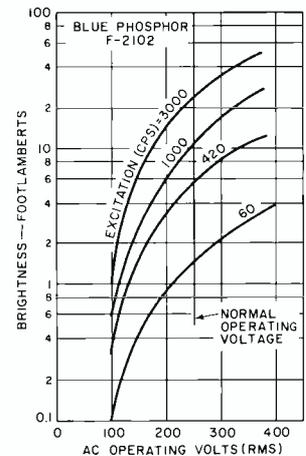
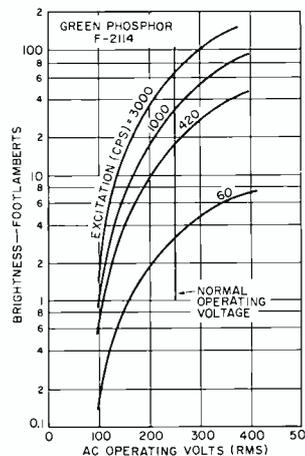


Fig. 6—Typical brightness characteristics of green EL phosphors (F-2114).



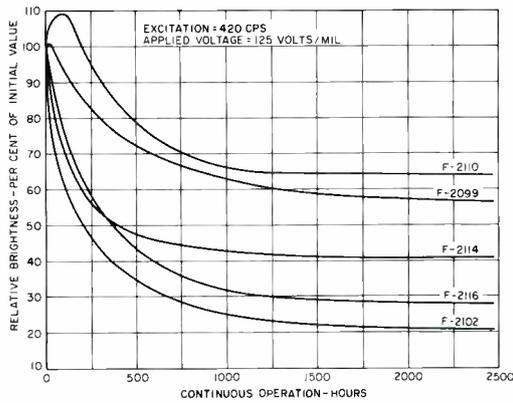


Fig. 10—Operating life of typical EL phosphors.

operating frequency increases, the rate of brightness decay increases, as shown in Fig. 11. Although operation at high frequencies yields a higher initial brightness, the brightness of a similar panel operated at a lower frequency may be higher after prolonged operation because it has a slower rate of deterioration. Voltage has a similar effect on life.

ADVANTAGES OF ELECTROLUMINESCENCE

Although some of the preceding statements may appear discouraging, there is no question that electroluminescence has definite advantages over other methods of lighting. For example, the type of light source used can be critical in certain applications. Incandescent and fluorescent bulbs are point and line sources, respectively. Electroluminescence is an area source of light. Provided that a low light level can be utilized, an area source of this type has the advantage of adaptability in shape. It can be fabricated into various shapes or forms. Panels as thin as 50 mils can be made for use

in applications where space is at a premium, such as in aircraft cockpits. Up to 200 incandescent or neon bulbs are presently used in such applications.

An additional advantage is that the electroluminescent light source is an integral part of the instrument and does not require additional space. Also, because the light emitted over the entire surface is uniform, observers are not bothered by shadows.

The life characteristics discussed previously can also be an advantage. Electroluminescent panels do not burn out with an immediate total loss of emission, as do incandescent bulbs. Their slow decay in brightness, therefore, provides a safety factor to protect against sudden loss of illumination on critical instruments. Another safety factor is the rugged construction of electroluminescent panels. They are not fragile, gas-containing bulbs, but sturdy panels which can be fabricated from plastics and metals. Even if the electrodes were damaged by severe blows, it would be possible for the undamaged parts to continue emitting. Electroluminescent light sources do not have to be rigid, but can be fabricated on flexible substrates or even on wires which can then be woven. These characteristics provide great potential for design engineers interested in the future of electroluminescence.

(The author thanks Dr. S. A. Harper for his helpful discussions and personal data.)

BIBLIOGRAPHY

1. D. Curie, *Journal DePhysique et le Radium*, Vol. 14; Pages 135, 5101, 672 (1953).

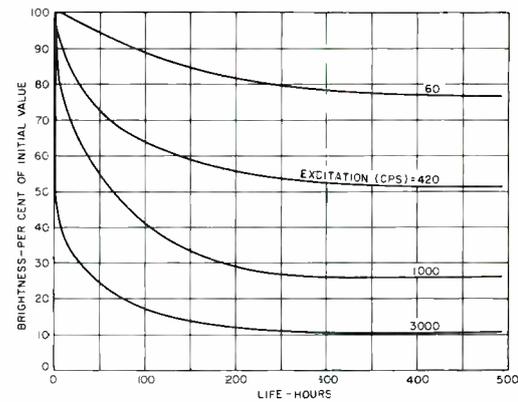


Fig. 11—Effect of operating frequency on life.

2. G. Destriau and H. F. Ivey, *IRE Proceedings*, Vol. 43; Page 1911 (1935).
3. W. W. Piper and F. E. Williams, *British Journal of Applied Physics, Supplement No. 4 Luminescence*, Page 539 (1955).
4. W. W. Piper and F. E. Williams, *Physical Review*, Vol. 98; Page 1809 (1955).
5. E. Nagy, *Acta Phys. Acad. Sri. Hung.* Vol. 6; Page 153 (1956).
6. C. H. Haake, *J. Opt. Soc. America*; Vol. 47; Page 881 (1957).
7. W. A. Thornton, *Optik*, Vol. 14; Page 319 (1957).
8. H. F. Ivey, *IRE Transactions on Component Parts*, Page 114 (1957).
9. W. W. Piper and F. E. Williams, *Vol. 6, Solid State Physics*, Page 96 (1958).
10. I. J. Hegyi, S. Larach and R. E. Shrader, *J ECS Vol. 104*; Page 717 (1957).



J. P. STANAVAGE received the B.S. degree in Chemistry from the University of Scranton in 1949. Prior to joining the RCA Lancaster Chemical and Physical Laboratory in 1954, he was employed by Allied Chemical Corp. and Pennsalt Chemical Corp. His major interest since that time has been electronically active solids, with particular emphasis on electroluminescence and photoconduction. Mr. Stanavage is a member of the American Chemical Society and the Electro-Chemical Society.

Fig. 7—Typical brightness characteristics of green-yellow EL phosphors (F-2099).

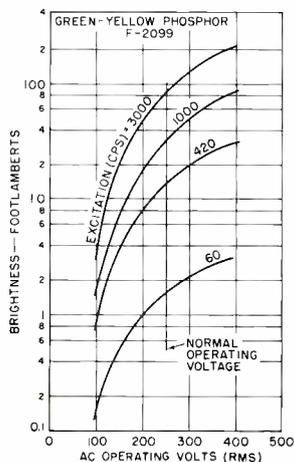


Fig. 8—Typical brightness characteristics of deep-yellow EL phosphors (F-2110).

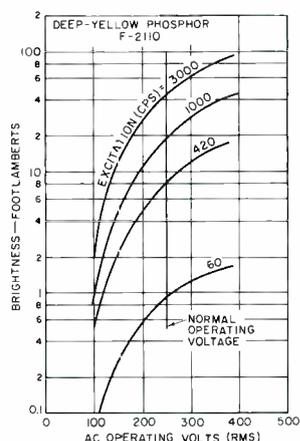
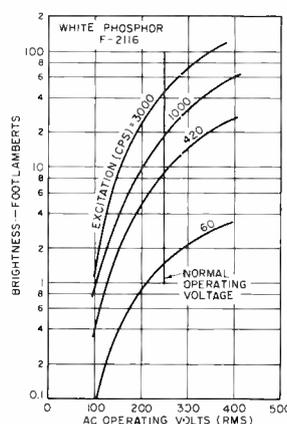


Fig. 9—Typical brightness characteristics of white EL phosphors (F-2116).



PHOTOCONDUCTIVE MATERIALS

by

Dr. G. S. BRIGGS and W. M. KRAMER

Chemical and Physical Laboratory
Electron Tube Division
Lancaster, Pa.

THERE IS A CONTINUING interest in the development of specialized photoconductive materials for use in devices having more-or-less complex configurations for various commercial applications. In many instances, the usefulness of the material depends on its ability to provide a photosurface of suitable size and configuration having the desired sensitivity, response time, and stability. This paper describes several materials used in commercial applications; the development of these materials reflects the cooperative effort of several engineering groups. Some of the techniques used in preparing photoconductive materials have also been useful in the preparation of other materials.

Three techniques are used in preparing large-area photosensitive layers: (1) *vapor deposition*, (2) the formation of polycrystalline layers by the *sintering* of adjacent particles on a suitable substrate, and (3) the use of *photoconductive powders* embedded in a suitable film-forming binder.

VAPOR DEPOSITION

The photosensitive surfaces presently used in vidicon-type camera tubes are evaporated from antimony trisulfide (Sb_2S_3 , Sb_4S_6) mixed with free sulfur, antimony, and/or other compounds. The fact that the photosurface is deposited by evaporation poses several special problems. The material to be vaporized must possess certain chemical and physical properties in addition to its necessary electronic properties. It must have a vapor pressure high enough so that it can be evaporated at a moderate temperature, yet low enough so that the material will not leave the photosurface during tube processing or use. The solid-phase transitions must be such that unwanted phase changes do not occur during tube processing or operation. The material should be capable of smooth evaporation without excessive evolution of gas or the spattering of liquid or solid particles which may cause spotlike imperfections on the photosurface. Chemically, it should be stable enough to undergo evaporation and subsequent exposure to the atmosphere without decomposition.

The base material, antimony trisulfide, may be prepared by either precipitation or elemental fusion. Precipita-

tion procedures yield a material of uncertain stoichiometry which evolves gas copiously during evaporation. Because of the difficulties encountered with precipitated material, several techniques have been devised for the preparation of antimony trisulfide by elemental fusion. The conditions for the preparation of antimony trisulfide by fusion methods are thermodynamically favorable at temperatures above its melting point.

Two methods of elemental fusion are now in use. The first, devised some years ago, is still used in producing commercial material. In this method, chemically pure antimony is mixed with somewhat less sulfur than is required to effect a stoichiometric compound. The charge is heated in an open Vycor tube under an argon atmosphere to a temperature of approximately 1000°C . As the reaction proceeds (violently at times) the melt is manually agitated, and additional lump sulfur is added until there is a considerable excess over that needed for stoichiometry. After a digestion period, the melt is cast into 7-mm sticks several feet long. In spite of the excess sulfur added, the material at this point is always found to contain excess antimony because sulfur volatility and the layering of the liquid phases during the digestion period prevent complete reaction.

A further refining step is, therefore, necessary. The sticks are fragmented and the free antimony is removed as completely as possible. The readily distinguishable differences in the crystal habits of the phases make this task pos-

sible with only visual inspection. The antimony trisulfide is then re-melted at 650°C under argon, digested, and recast as before. During this digestion period, the excess, undissolved antimony settles out because the antimony has a considerably higher density than antimony trisulfide. The amount of free antimony in solid solution (and precipitated in the solid mass) is a function of the digestion temperature and the rate of cooling of the cast sticks. The freezing-point curve of the antimony trisulfide-antimony system shown in Fig. 1 indicates that lower digestion temperatures decrease the percentage of antimony until the eutectic is reached at 73.3 percent. Material containing less than this percentage cannot be made by this method. In practice, this eutectic is not readily obtained because of the prolonged period needed to attain equilibrium. As a result, the finished material varies in composition from 74- to 78-percent antimony.

Another method was developed to overcome the composition difficulties in the previous method and to provide a purer material. The sulfur used is distilled, and the first and last fractions are discarded. Special antimony of 99.9999-percent purity is purchased as pound ingots, which are fragmented as needed to minimize contamination. The desired amounts of antimony and sulfur are weighed into Vycor tubes, which are then evacuated, sealed, and loaded into iron tubes. The iron tubes are then placed in a compartmental muffle furnace, as shown in Fig. 2. The furnace is program-controlled and is so designed that the charge is slowly rotated end-over-end during the entire firing schedule. This method effectively prevents the formation of nonreactive layers and permits the reaction to proceed at a slow, nonviolent rate. With this system, approximately six hundred grams of material can be prepared per firing. After cooling, the tubes are broken open, the Vycor is removed, and the antimony

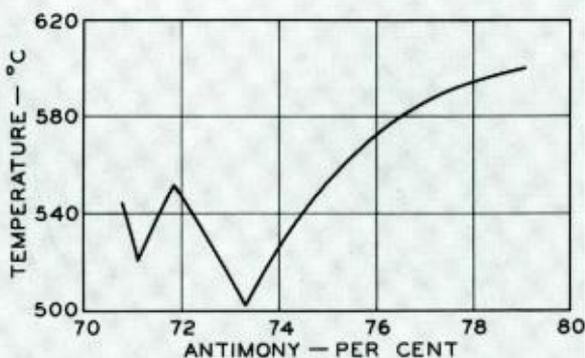


Fig. 1—Freezing-point curve: antimony trisulfide (Sb_2S_3)/antimony system.

trisulfide is ground and screened to the desired size. This method is effective for the preparation, not only of antimony trisulfide photoconductors of various compositions, but also of other high-purity materials.

This method of preparation promises to become an important tool in the control of photosurface compositions. Because the vidicon photosurface is prepared by evaporation from an antimony-antimony trisulfide mixture, there are a number of variables in its preparation which are beyond the scope of this paper. The composition of the photosurface is controlled by the interrelationship of several factors—the composition, temperature, and degree of decomposition of the mixture during evaporation, the resulting vapor pressure of the component materials of the mixture, the accommodation coefficient of the substrate for the various species in the vapor stream, and the ambient pressure in the evaporation chamber during the evaporation.

If the photosurface could be prepared with no other considerations than that of composition, the problem—though not simple—would be far less complex. Unfortunately, each of the factors controlling composition also controls physical properties of the photosurface which are equally important in their effect upon the electrical properties of the photosurface. None of the chemical effects have been independently evaluated as yet, although some progress has been made. The temperature-vapor pressure relationship of antimony trisulfide from 551 to 600°C is shown in Fig. 3. A comparison of this curve with that of antimony indicates, in the ideal case, that the lower the temperature of a given evaporating material the richer the vapor in antimony. This relationship is based on a variation of Raoult's law, which shows that the ratio of two components in the vapor phase is equivalent to N_1P_1/N_2P_2 , where N_1 and N_2 are the respective mole fractions of each component in the system, and P_1 and P_2 their vapor pressures. It is desirable that the thermodynamic properties of the antimony-antimony trisulfide system be known so that the temperature of the evaporating material may be varied according to the requirements of other characteristics.

PHOTOCONDUCTIVE SINTERED LAYERS

Large-area sintered photoconductive layers of cadmium sulfide (CdS) and cadmium selenide (CdSe) are presently being used in several commercial devices. These layers, or materials, are particularly interesting because they have sensitivities (microamperes per

lumen) of the same order of magnitude as single crystals of comparable composition. These sintered layers are prepared as follows: a desired mixture of raw materials is spray-coated on a substrate, and the coating is then fired to re-crystallize the host material in a molten solvent. The firing process incorporates the desired impurities in the host material and then evaporates the solvent.

Spray Preparation and Application

The CdSe (or CdS) spray suspension is prepared as follows: CdSe, CdCl₂, and CuCl₂ in suitable proportions are added to a measured quantity of demineralized water, and the mixture is ball-milled overnight. Variations in the proportions and purity of the constituents, as well as the particle size of the CdSe, are important factors in the characteristics of the resulting photoconductive layer.

Although CdSe may be prepared by precipitation from salt solutions with H₂Se, by solid-state reaction between precise amounts of CdO (3 mols), CdS (0.9 mol), and Se (3 mols) in an inert atmosphere, or by the direct reaction of Cd and Se under vacuum at elevated temperatures, the quantities of material available by these techniques have been limited and have had variable purity. The CdSe presently used is a commercial product prepared by precipitation from solutions of cadmium and an organoselenium complex; it is of good uniformity and purity and has a maximum particle size of about one micron, but a purer grade of CdSe is needed.

The CdS, on the other hand, is RCA high-purity phosphor-grade precipitated material. The cadmium chloride and CuCl₂ used are reagent-grade chemicals.

The preferred method for applying the CdSe suspension to the substrate is spraying. The texture of the coating, whether it be porous or dense (i.e., a dry or wet deposit), may be modified by control of the spray volume and/or gun-to-work spacing for any given particle-size spray suspension. Deposits by sedimentation in aqueous media were unsuccessful because of the poor wet strength of the coatings. Coatings deposited from organic suspensions such as acetone and some of the lower alcohols had good coverage with fair wet-adherence and provided useful photoconductive layers when sintered.

Because the sintered layer requires a supporting surface which is substantially inert throughout the entire processing, dense, high-fired ceramic materials containing at least 85 percent of alumina by weight appear to be most desirable. Certain borosilicate glasses (#774 and #7052), however, have also been used successfully as substrate materials. The least stable coatings were those prepared on lime glass; the glass eroded badly during firing, probably because of the chloride content of the spray and the sintered layers had dark currents orders of magnitude greater than comparable surfaces on high-alumina ceramics with light-to-dark-current ratios usually less than ten. Table I shows the photoconductivity of CdSe layers on various substrates.

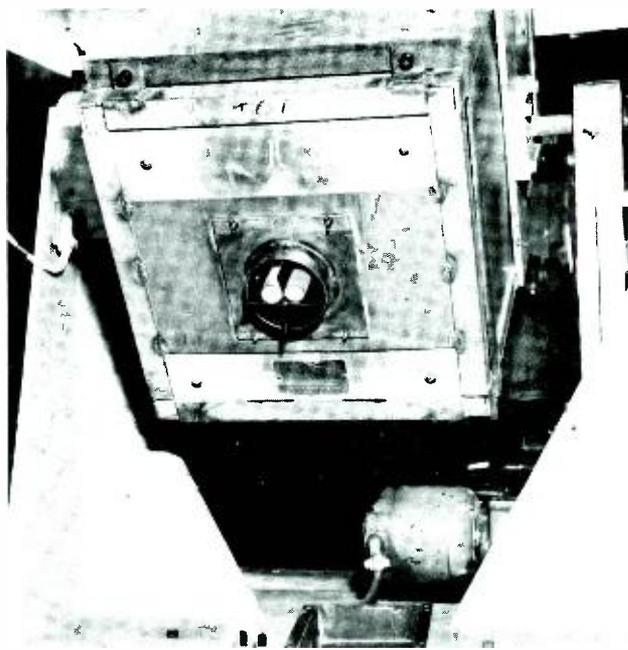


Fig. 2—Compartmental muffle furnace used in preparation of antimony trisulfide (Sb₂S₃).

Coatings sintered on soft glass containing lead were highly resistive and showed no photosensitivity, presumably because of the poisoning effect of the lead on these materials.

Coating Processing

The formation and continuity of the CdSe and CdS layers, after firing, are intimately associated with the CdCl₂ content of the coating, the coating porosity, and the firing conditions. Without CdCl₂ it is not possible to make sintered layers of CdSe and CdS. The CdCl₂ acts as a solvent-flux that knits the CdSe and CdS aggregates together without destroying their structure; it acts as a source of donors (the chloride ion), and promotes the incorporation of copper into the crystal lattice.

Both CdSe and CdS are soluble in molten CdCl₂ to about 40 and 30 percent, respectively. Because of this relatively high degree of solubility, it is necessary to control the level of CdCl₂ in the coating carefully to prevent complete solution during firing. If complete solution of the CdSe and CdS occurs, the texture of the layer is destroyed and, on cooling, discrete crystallites of sulphide and selenide form from the melt, leaving a heterogeneous layer. Under certain conditions, prolonged firing produces layers which are "glassy" and homogeneous in appearance. In both instances, the layers are highly resistive and show no photoconductivity. If, however, less than 10 percent but more than 2 percent of CdCl₂ by weight is added to the coating and the firing conditions are optimum, a continuous polycrystalline layer is formed. It appears, therefore, that the controlled amount of melted CdCl₂ dissolves only the smallest crystallites and the peripheral areas of the larger CdSe and CdS particles during the firing cycle. After cooling, a continuous polycrystalline layer of CdSe and CdS forms. Variations in processing affect the extent of this zone, or intergranular area, and its composition. Free CdCl₂ evaporates during the firing cycle. Although the melting point of CdCl₂ is at a temperature of 568°C, the solution of CdSe and CdS lowers the melting point to a temperature of about 500°C. This effect explains why sintering may be obtained at the lower temperature. Although coating density and porosity are modified by the particle size of the CdSe (or CdS) and the method of application, these factors are less important in determining the continuity and properties of high-CdCl₂ sintered layers than of coatings containing less than 5 percent of CdCl₂ by weight. The former layers are prone to "mud-cracking," probably because of non-uniform distribution of

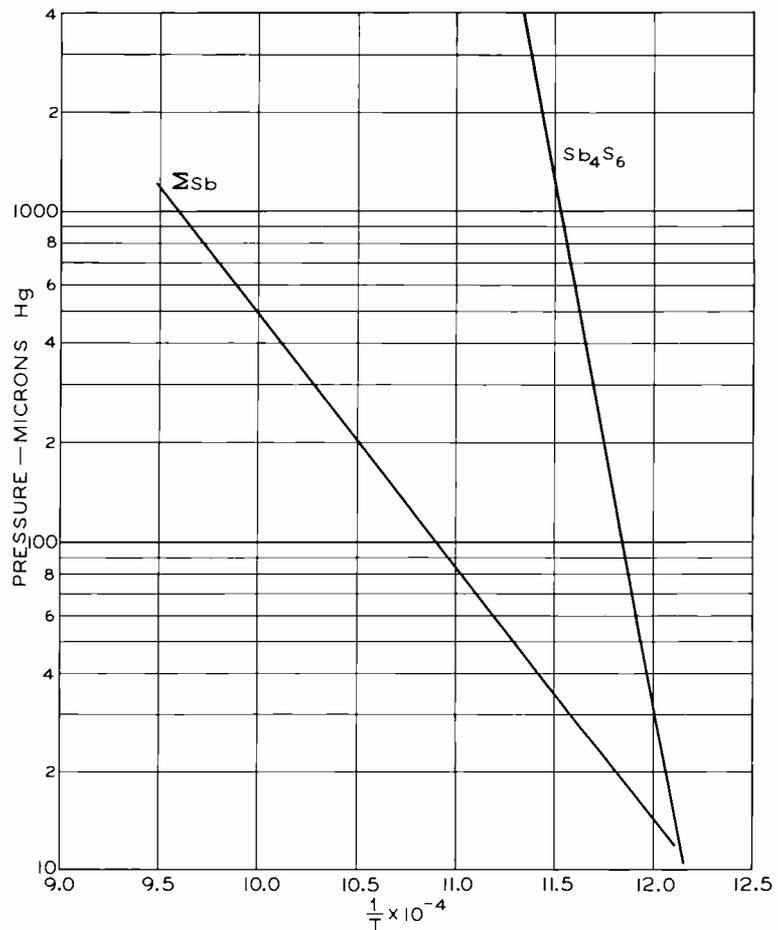


Fig. 3—Vapor pressure—temperature relationship for antimony and antimony trisulfide (Sb₂S₃).

CdCl₂ and greater solution of the CdSe (or CdS). Low-CdCl₂ layers are more continuous. Firing time and temperature are more critical with low-CdCl₂ sprays than with high-CdCl₂ sprays. Excessive loss of CdCl₂ by evaporation prior to reaching the sintering temperature precludes any possibility of sintering.

Early in the investigation of sintered-layer formation, it was observed that slight changes in the firing procedure of coatings having the described composition had a marked effect on the photoconductivity of these layers. These effects are shown in Table II.

In the absence of air, the CdSe sintered layer shows low resistivity with essentially no photoconductivity. The addition of air or oxygen increases resistivity, and the sintered layers become photoconductive. Only partial sintering of the coating occurs in the absence of air. Furthermore, appreciable turbulence appears to decrease the completeness and extent of sintering, presumably by *sweeping* away the CdCl₂ before its function as the recrystallizing medium or solvent for the CdSe (or CdS) can be accomplished. It was further observed that not only is a par-

ticular, stagnant atmosphere required around the CdSe coating but the volume of the gaseous surround should be minimized. The firing procedure itself is most critical in its effect on sintered-layer characteristics. For example, when the rise time to furnace temperature was 5 to 8 minutes, electroded sintered layers at 0.1 foot-candle provided 31 microamperes current; at zero foot-candles, 0.01 microampere. Comparable layers fired with a rise time of 11 to 14 minutes gave one-third less photocurrent with no change in dark current under similar test conditions.

The useful temperature range for sintering CdS and CdSe layers is between 480 and 600°C. Obviously, shorter firing times are required at the higher temperatures.

In addition to its action as a sintering agent (solvent), CdCl₂ acts as a source of donors, either by incorporating chloride into the crystal lattice or by forming a non-stoichiometric excess of cadmium. Thus, in the absence of copper, sintered layers prepared as described have low resistivity but show no photosensitivity.

Although copper is added to the spray suspension as the chloride, it immedi-

ately becomes converted to copper selenide and is present in the suspension and on the dried coating in this form. During the firing of the coated substrate, the melted CdCl₂ dissolves the peripheral areas of the CdSe (and CdS) particles, as previously described, on which the copper selenide has precipitated. The resulting continuous phase containing cuprous copper forms the completed photoconductive polycrystalline layer. Photoconductivity is thus attained by introducing acceptors such as copper to compensate partially for the added excess donors. As the concentration of copper is increased, there is a change of resistivity under illumination. The concentration of copper and chloride is, thus, an important factor in determining the electrical properties of the sintered layer.

PHOTOCONDUCTIVE POWDERS

Photoconductive powders of CdS (and CdSe) have been prepared from purified CdS (and CdSe) by a two-step or three-step firing method in which chloride and copper are incorporated. The critical parameters are essentially the same as those outlined for sintered-layer preparation; the CdCl₂ is the all-important flux which permits the growth of discrete uniform crystallites and the incorporation of chloride and copper into the lattice. Bulk firing is used for powder preparation. Because CdCl₂ is water-soluble, the fired lumps readily disintegrate in water and provide a powder of uniform particle size. Subsequent firings in chloride and sulphur atmospheres determine final powder characteristics by control of the copper and chloride content. These free-flowing photoconductive powders may then be incorporated in a film-forming binder for the desired application. Care must be exercised in binder selection, however, to ensure chemical neutrality and stability of the photoconductive powder.

SUMMARY

In the preparation of certain broad-area photoconductive layers (evaporated films, sintered and powder coatings), it was observed that the stoichiometry and the proportion and type of impurities present, the composition of the substrate, the density of the preferred coating, the nature of the atmosphere used during the formative process, and the time and temperature of firing have a profound effect on the photoconductivity of the resulting layer. Although the effect of these factors on the electrical characteristics of the photoconductive layer is apparent, improvement of its properties by material modifications and process changes is not readily accomplished.

TABLE I—Photoconductivity of CdSe Sintered Layers on Various Substrates (Tubes Fired in N₂+air)

| Substrates | Microamperes* | |
|-----------------------------------|------------------|--------------------|
| | (0 foot-candles) | (0.1 foot-candles) |
| Glass | | |
| Borosilicate | 0.11 | 86 |
| Lime glass | 9.0 | 104 |
| Vitreous Ceramics | | |
| 85% alumina | 0 | 54 |
| Zirconium silicate | 0 | 29 |
| Zirconium silicate: mullite | 0 | 5 |

* Measurements made at a dc voltage of 9 volts with a gap 1/16" x 3/8".

TABLE II—Photoconductivity of Cadmium Selenide Sintered Layers Prepared in Various Atmospheres

| Atmosphere | Tube Firing | | Microamperes† | |
|-----------------------|------------------|----------------|-----------------|-------------------|
| | Temperature (°C) | Time (minutes) | (0 foot-candle) | (0.7 foot-candle) |
| N ₂ P.P. * | 600 | 5 | 500 | 600 |
| A P.P. * | 600 | 5 | 10,000 | |
| He P.P. * | 600 | 5 | 280 | 290 |
| N ₂ + Air | 600 | 5 | 0.02 | 500 |

* Slight positive pressure maintained.

† Measurements made at 5 volts; gap width 1/16" and length 3/8".



DR. GEORGE S. BRIGGS received the B.S. degree from Northwestern University in 1933 and the Ph.D. in Science from Rutgers University in 1940. He has been employed by RCA since 1942, except for a fifteen-month service in the U. S. Department of Agriculture. At RCA, his fields of interest have been electroplating, vacuum tube chemistry, and photoconductor materials. He is presently a senior engineer in the Semiconductor Photocell Design activity of the Electron Tube Division in Lancaster. Dr. Briggs is a member of the American Chemical Society and Sigma Xi.



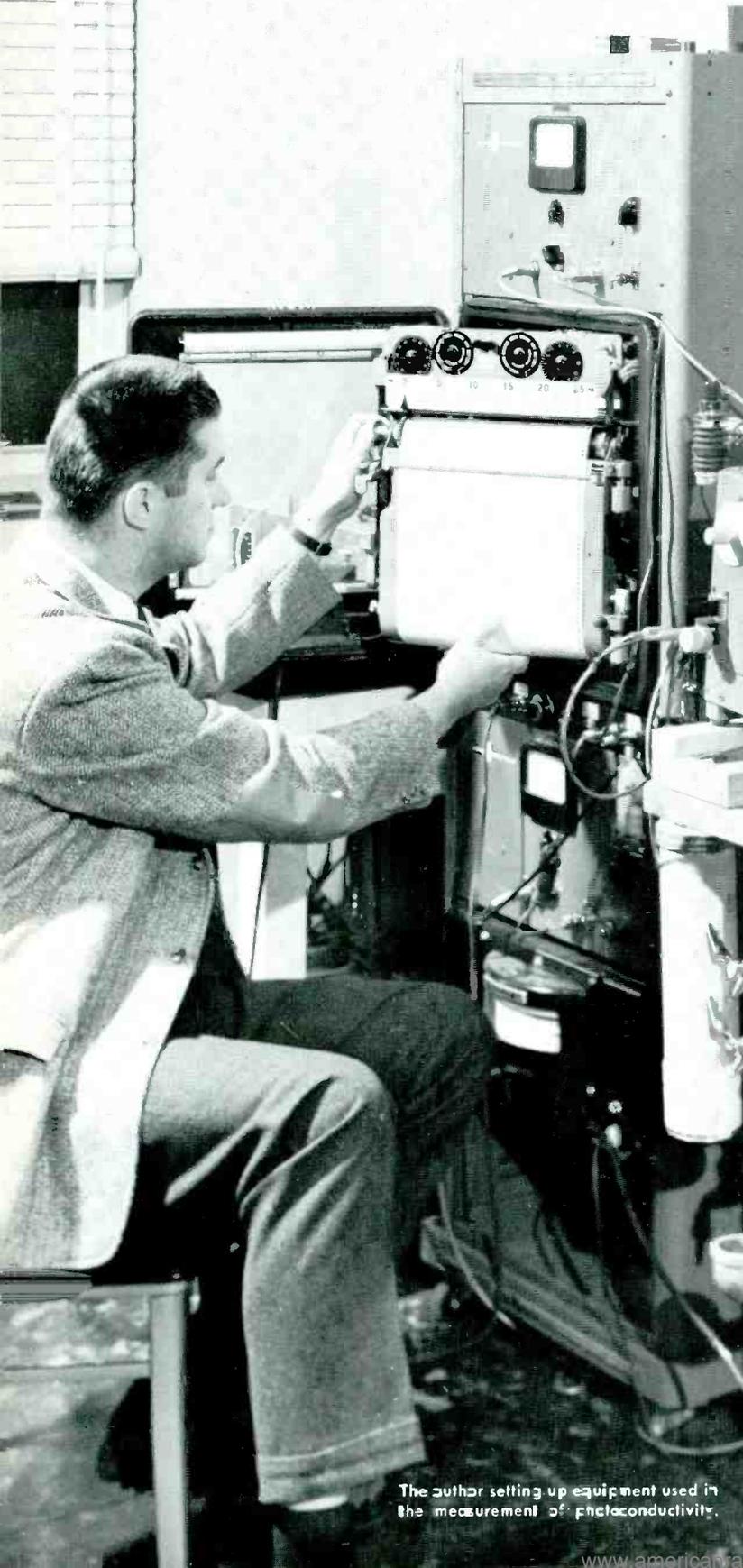
WILLIAM M. KRAMER received the B.S. degree in Chemical Engineering from West Virginia University in 1942. He entered the U. S. Navy in 1942 and served in the Submarine Forces, Pacific Fleet. At the end of the war he became associated with the Adamston Flat Glass Company as Chief Chemist. In 1957 he joined the Chemical and Physical Laboratory of the Electron Tube Division in Lancaster, and shortly thereafter was assigned to the development of specialized photoconductors for use in vidicons and solid-state devices.

PHOTOCONDUCTIVITY

By

Dr. R. H. BUZE

*Physical and Chemical Research
RCA Laboratories
Princeton, N. J.*



The author setting up equipment used in the measurement of photoconductivity.

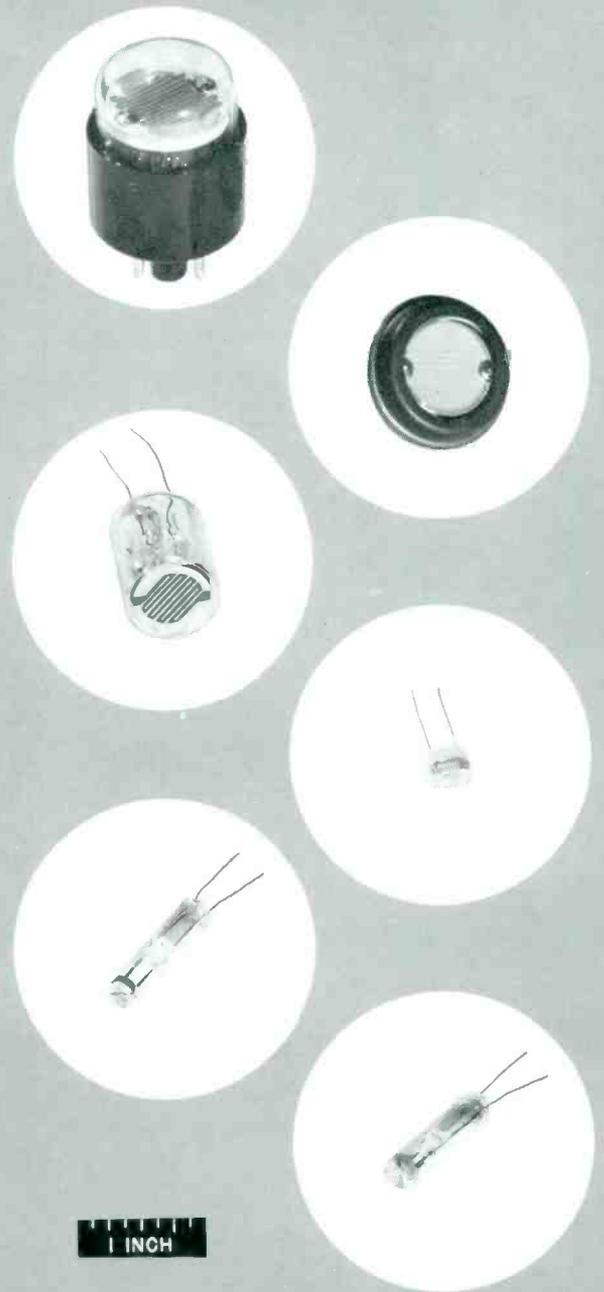


Fig. 1—Commercial or developmental (prefix C) photoconducting cells now being produced by RCA. From Top to Bottom: CdS sintered-layer, glass-enclosed Cell 6957; same layer, metal-enclosed Cell 7163; CdSe sintered-layer, glass-enclosed Cell C7218; single-crystal CdS Cell 6694A; CdSe sintered-layer Cell C7230; CdS sintered-layer Cell 7412. These cells, because of their incorporated impurities, are sensitive over a wide range of wavelengths: CdS cells, 0.33 to 0.74 μ ; CdSe cells, 0.35 to 0.87 μ . Sensitivity lies in the range of amperes per lumen, about one-tenth that obtainable with a multiplier phototube such as the 931A.

A PHOTOCONDUCTOR IS A material whose electrical conductivity can be increased by the absorption of light or other suitable radiation. Thus, photoconductors are useful both as radiation detectors (ultraviolet, visible, infrared, electrons, X rays, gamma rays, nuclear particles) and as radiation-controlled electrical switches.

Although photoconductivity was first discovered in 1873 by Willoughby Smith while investigating selenium as a resistor in underwater cables, actual progress in understanding and material development has awaited the recent leap forward in all solid-state physics which was activated by the development of the transistor. Photoconducting cells were made only of selenium, copper oxide, or thalious sulfide up to 1940; today, commercial cells use none of these, but are based almost exclusively on germanium, silicon, cadmium sulfide, cadmium selenide, lead sulfide, lead selenide, or lead telluride, all resulting from recent developments. It was not until the end of World War II that detection of infrared radiation by the lead-sulfide-type photoconductors proved superior to former thermoelectric or bolometric methods. Fig. 2 shows the intrinsic photoconductivity response as a function of incident wavelength for a number of typical photoconductors.

In many cases, photoconducting cells today perform the same functions previously performed by photoemissive cells, with the advantages of decreased size and cost, and increased ease of operation. The solid-state photoconductor cell bears the same relationship to the photoemissive vacuum phototube as the solid-state diode bears to the thermionic-emissive vacuum diode. The photoconducting television camera tube, the *vidicon*, is partially replacing the photoemissive tube, the *image orthicon*. Photoconductors currently play a role also in computers and a whole host of detection and control systems, including street-light control, headlight control and dimming, camera-iris setting, and automobile rear-view mirror orientation. At the developmental level, photoconductors are a part of experimental picture-display and light-amplifier systems, where the properties of the photoconductor are beneficially combined with those of electroluminescent materials. Photoconductivity itself is one of the basic tools of solid-state research, being used to determine carrier lifetime, carrier mobility, trapping phenomena, imperfection-level location, and capture cross-sections of imperfection centers for free carriers.

Research in photoconductivity embraces a wide area of chemistry,

physics, crystallography, and metallurgy. Photoconductors may be inorganic or organic, insulators or semiconductors, crystalline or amorphous; they may be used in the form of single crystals or microcrystalline powders; thin sintered, evaporated, chemically deposited, or sputtered layers; or thick sintered pellets.¹

In this paper we shall concentrate mainly on the physical processes underlying photoconductivity and the applications which have been made of the phenomenon. A reasonable start has been made at developing a phenomenological theory of photoconductivity, but a considerable portion of the preparation of useful cells still lies in the realm of synthesis art.

Fig. 1 shows several photoconducting cells utilizing cadmium sulfide or cadmium selenide as the photoconducting material. What we shall say here is directly applicable to this type of photoconducting material, and with certain appropriate modifications, to other types of material as well.

CHARACTERIZING PROPERTIES

There are four properties of a photoconductor (together with their variation with excitation intensity and temperature) which serve to characterize it: (1) *dark conductivity*, (2) *spectral response*, (3) *speed of response*, and (4) *photosensitivity*. Fig. 3 and 4 should be consulted as a background to the following discussion.

Dark Conductivity

The conductivity in the dark depends on the band gap of the material, and on the density and type of imperfections which are present. In insulators (room-temperature conductivity less than about 10^{-6} /ohm-cm) the density of free carriers in the dark because of thermal excitation is usually much less than the density of free carriers created by photoexcitation. In semiconductors (conductivity greater than 10^{-6} /ohm-cm, but less than 10^2 /ohm-cm) the density of free carriers in the dark is usually greater than the density of photo-excited carriers. This intrinsic difference between insulators and semiconductors affects not only some aspects of their photoconductivity behavior, but also the conditions under which photoconducting cells are used. Insulating photoconductors are usually operated at room temperature with steady radiation. Semiconducting photoconductors are usually operated at low temperatures with intermittent radiation to produce an alternating signal suitable for amplification.

Spectral Response

In a pure material, light of energy less than the band gap cannot create free carriers, and therefore cannot give rise to photoconductivity. Photoconductivity results from excitation by light of energy equal to or greater than the band gap (Fig. 3, transition 1), and ceases abruptly when the energy of the light decreases to a value smaller than the band gap. Actually, a maximum response is usually found at a light energy very close to that of the band gap; the decrease in response for higher-energy light results from the complete absorption of this light in surface regions of the photoconductor which have an intrinsically lower photosensitivity than the volume.

When imperfections are present (Fig. 3, transition 2), less energy is required to excite an electron from the imperfection level to the conduction band than is required to excite across the band gap. The presence of such imperfections shows up therefore as additional response for light of energy less than the band gap, i.e., as a response to the long-wavelength side of that associated with the pure material. The lowest-energy light able to give the imperfection response serves to locate the level with respect to the bottom of the conduction band.

Speed of Response

Trapping centers are those which temporarily remove electrons from the free state and then return them to the free state at a later time when sufficient thermal energy has been supplied from crystal vibrations (Fig. 3, transitions 5 and 6). In a material with no trapping effects, the speed of response would be identical with the lifetime of the free electrons. In actual practice, particularly for low-light-intensity excitation, the observed speed of response is many orders of magnitude less than would be expected from the lifetime. The occurrence of these rise and decay times much greater than the lifetime is caused by trapping of free carriers. Trapping lengthens the rise time by removing photoexcited free electrons from the free state and requiring a time elapse for a steady state to be set up between the new density of free electrons and the new occupancy of trapping centers. Trapping lengthens the decay time by slowly releasing trapped electrons after the excitation has been terminated. In the case of low-intensity excitation, the density of trapped electrons may greatly exceed the density of free electrons, so that the decay time is really given by the time required to free an electron from a trap, rather than by the free lifetime

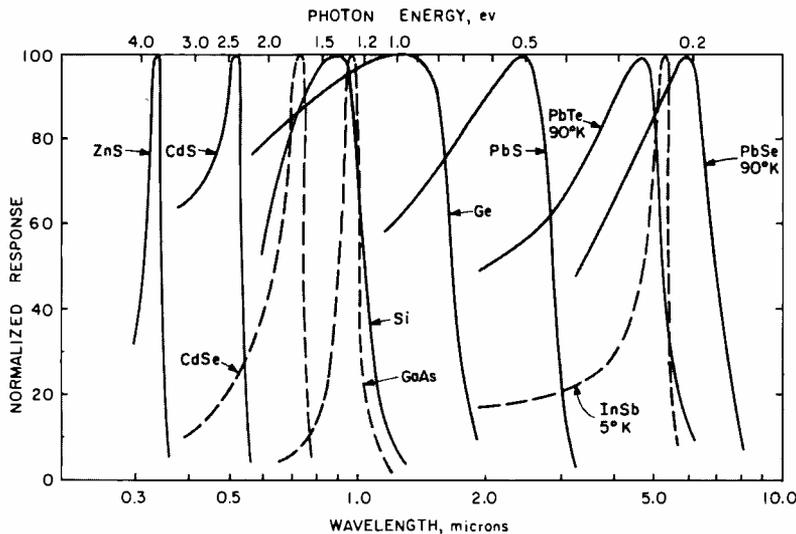


Fig. 2—Intrinsic photoconductivity response of typical photoconductors vs. wavelength, where "intrinsic" means response of the material itself without incorporated impurities. Impurities extend response to longer wavelength than the intrinsic response. Intrinsic responses extend from the ultraviolet ($<0.4\mu$) through the visible (0.4 to 0.7μ) into the infrared ($>0.7\mu$).

determined by recombination between a free electron and a hole captured at a recombination center.

Photosensitivity

The value assigned to the photosensitivity of a photoconductor should express how useful the photoconductor is in converting light energy into electrical current. There are at least three ways of defining this utility which are in common use.

(1) *Minimum detectable excitation required to give a signal equal to the noise.* This definition of sensitivity is applied principally to detectors of infrared radiation, like lead-sulfide photoconductors. The minimum detectable excitation, expressed in terms of radiation power, is about 10^{-12} watt to give signal equal to noise in such photoconductors.

(2) *Photocurrent per unit light intensity at fixed applied field.* This definition of sensitivity has been called specific sensitivity, and has been expressed in units of $\text{cm}^2/\text{ohm-watt}$. It is obtained by multiplying the conductance by the square of the electrode spacing and dividing by the total radiation power absorbed.

$$\text{Specific Sensitivity } S \equiv \frac{\Delta i}{V} l^2 \quad (1)$$

where Δi is the photocurrent, V is the applied voltage, l is the electrode spacing, and P is the absorbed radiation power. The specific sensitivity is independent of cell geometry or light intensity, provided that the photocurrent varies linearly with applied field and

light intensity. The most sensitive cadmium-sulfide and cadmium-selenide photoconductors have specific sensitivities near unity. The sensitivities of several forms of cadmium sulfide are summarized in Table I.

(3) *Photoconductivity gain, i.e., the number of electrons passing between electrodes for each photon absorbed.* This definition is perhaps the most useful for many practical considerations. An analysis of the effects described in Fig. 4 shows that this gain can be expressed:²

$$\text{Gain} = \frac{\text{Lifetime of free electron}}{\text{Transit time of free electron}} \quad (2)$$

If τ is the lifetime of a free electron, and if we express the transit time of a free electron between electrodes separated by a distance l as this distance divided by its velocity, then

$$\text{Gain} = \frac{\tau \mu V}{l^2} \quad (3)$$

where μ is the electron mobility, and V is the applied voltage. Gains of 10^4 have been observed in cadmium sulfide cells.

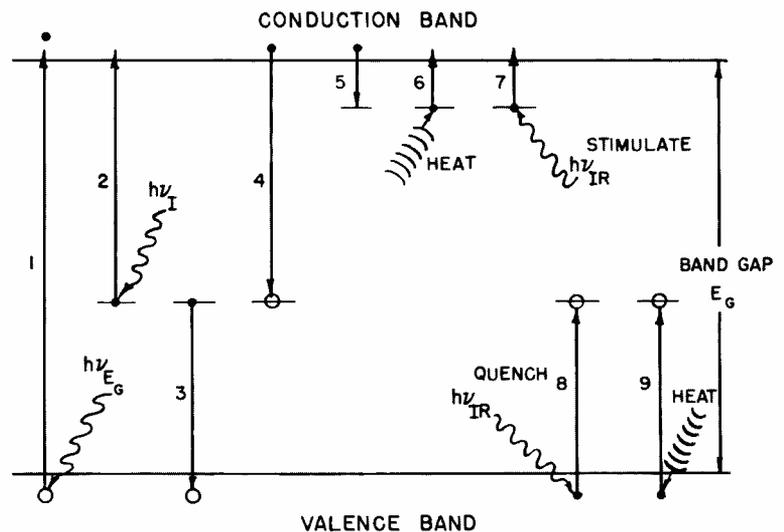
**Lifetime—
Key Photoconductivity Parameter**

It is evident from Eq. (3) that the $\tau \mu$ product forms a kind of figure of merit for a photoconductor. The mobility μ is more or less fixed by our choice of material, but for any given material the lifetime τ can vary over wide limits. In insensitive cadmium sulfide, the electron lifetime is of the order of 1 microsecond, whereas in sensitive cadmium sulfide the electron lifetime is of the order of milliseconds. The lifetime τ itself depends on the recombination process (Fig. 3, transition 4) in the following way:

$$\tau = \frac{1}{v S_n N_r} \quad (4)$$

Here N_r is the density of recombination centers, i.e., the density of those centers which have captured photo-excited holes. S_n has the dimensions of area and is called the capture cross-section of these centers for free electrons. v is the thermal velocity of a free electron.

The product $v S_n$ represents the total volume swept out in one second by a recombination center. The magnitude of the capture cross-section depends directly on the chemical nature of the



center. A center with a Coulomb attraction for the carrier under consideration has a capture cross-section of about 10^{-13} cm². A neutral center has approximately a geometric cross-section of 10^{-15} cm². Centers which are charged such that there is a Coulomb repulsion of the carrier under consideration may have cross-sections as small as 10^{-20} cm². Each imperfection center is characterized by two cross-sections: one for holes and one for electrons. Quite often these two cross-sections are widely different: in sensitive cadmium sulfide crystals, for example, the capture cross-section of centers B for holes is 10^6 time larger than the capture cross-section of these centers for electrons (after a hole has been captured).³

Maximum Performance

Assuming that the material parameters τ and μ have been fixed, the photoconductivity gain of Eq. (3) can still be increased by increasing the applied voltage or by decreasing the electrode spacing. Although Eq. (3) indicates no limit to which such an increase can be pushed, there are three physical phenomena which will terminate the applicability of Eq. (3) under the continued increase of applied field. These are (1) the injection of space-charge-limited current from the cathode, (2) impact ionization by free carriers, and (3) dielectric breakdown. Injected space-charge-limited current is usually encountered first with increasing applied field. Maximum gain is reached at that applied voltage at which the injected current is approximately equal to the photocurrent. Traps play a dual role: they give rise to long response times by

filling and emptying during photoexcitation, as mentioned previously, but they also allow the achievement of higher maximum gain by increasing the maximum field which can be applied before space-charge-limited currents become important. Traps bring about the latter effect by capturing the injected carriers.

the captured hole. In general, two types of centers can capture holes, indicated as centers A and B. Centers A have a large probability of capturing a free electron after having captured a hole; centers B have a small probability of capturing a free electron after having captured a hole. Centers A exist in all crystals of CdS, even the purest prepared to date; since they aid recombination, they cause low photosensitivity. If centers B are added deliberately, a sensitive photoconductor is produced; the net result of adding centers B is to reduce the number of centers A available for recombination by essentially keeping the centers A occupied by electrons.

Fig. 4—A photoconductor in operation, here specifically for an n-type photoconductor like CdS. Two ohmic metallic contacts to the photoconductor are assumed. 1) Absorption of a photon forms a free electron-hole pair. 2) Under the applied electric field, the photo-excited electron moves toward the anode. 3) Similarly, the photon-excited hole moves toward the cathode. 4) The hole is captured at an imperfection center. 5) After the initial electron has left the photoconductor at the anode, the residual positive space charge due to the excess captured hole leads to the entrance of an electron into the photoconductor from the cathode. Photocurrent continues until a free electron recombines with

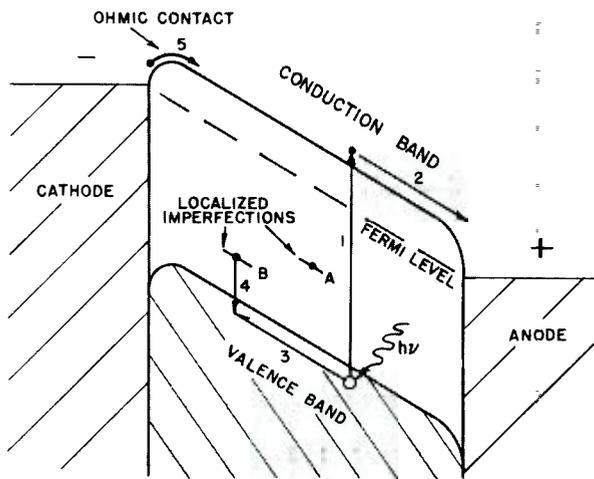


Fig. 3—Basic electronic processes in a photoconductor, here specifically for an n-type photoconductor like CdS. (Arrows indicate electron transitions.) 1) Excitation of host crystal by absorption of light with energy equal to or greater than the band gap; for each photon absorbed, one electron-hole pair is formed. 2) Excitation of a bound electron at an imperfection level; imperfections may be either impurities or crystal defects such as vacancies. 3) Capture of a photo-excited hole by an imperfection center. 4) Capture of a photo-excited electron by a center which has previously captured a photo-excited hole, resulting in recombination of the carriers. 5) Capture of a photo-excited electron by an electron-trapping center. 6) Thermal freeing of a trapped electron. 7) Optical freeing of a trapped electron. 8) Optical freeing of a captured hole. 9) Thermal freeing of a captured hole. Transitions 1 and 2 determine spectral response; 3 and 4 determine free-electron lifetime and, hence, photosensitivity; 5 and 6 frequently determine speed of response; 7 causes stimulation of conductivity; 8 and 9 correspond to optical and thermal quenching of photoconductivity when the centers involved are those with small cross-section for free electrons. Transitions 3 and 4 may be either radiative, i.e., give rise to luminescence emission, or nonradiative.

An expression for the maximum gain as limited by current injection has been derived:⁴

$$G_{max} = \frac{\tau_o}{\tau_{RC}} \frac{N_A}{N_t} \quad (5)$$

Here τ_o is the observed response time, τ_{RC} is the product of the resistance R and the capacity C under operating conditions, i.e., the RC time constant or the dielectric relaxation time, N_A is the number of positive charges on the anode corresponding to the number of traps filled by the field-injected current, and N_t is the number of traps filled by the photoexcitation process (including the free electrons in N_t).

If the same traps are filled both by field-injected charge and by photoexcitation, then $N_A/N_t = 1$, and the maximum gain is limited to unity for many applications for which $\tau_o \approx \tau_{RC}$, such as the vidicon or the light amplifier. If, however, there are centers which are filled by field-injected charge, but are not filled by photoexcitation, the maximum gain^{5,6,7} can exceed τ/τ_{RC} . Recombination centers (centers B) lying at the proper place in the forbidden gap (just above the Fermi level) meet these requirements. Alternatively, surface traps may capture the injected charge while photocurrent flows primarily through

volume regions with a such smaller trap density.

Maximum practical performance of a photoconductor cell requires maximum G_{max}/τ_0 , or maximum gain-bandwidth product. For a typical case of a sandwich-type cell, we can express this product:

$$\frac{G_{max}}{\tau_0} = Kn \frac{N_A}{N_t} \quad (6)$$

where K is a constant depending only on the dielectric constant and the electron mobility of the photoconductor, and n is the density of free electrons. The gain-bandwidth product can therefore be maximized in three ways: (1) increasing the operating conductivity, (2) increasing the density of centers which capture field-injected charge but not photo-excited charge, and (3) decreasing the density of centers which capture photo-excited charge, i.e., the conventional electron trapping centers. The first of these is often ruled out since many applications of photoconductors have a maximum allowable conductivity. Both of the other alternatives involve appreciable difficulty in synthesis.

SUMMARY

This is the situation in photoconductivity today. Present research has met with some success in decreasing the density of trapping centers by careful control of purity and preparation, and scattered crystals have shown photoconductivity performance indicating values of N_A/N_t as high as 500. Table I compares the low-light speed of response of such

TABLE I Properties of Various Cadmium Sulfide Photoconducting Materials

| Material | Specific Sensitivity, $cm^2/ohm\ watt$ | Electron Lifetime, sec.* | Response Time at $10^{-4}\ ft-c$, sec. |
|--|--|--------------------------|---|
| Impure CdS (Contains recombination centers such as Ni) | 10^{-9} | 10^{-10} | — |
| Pure CdS (No spectrographically detectable impurities) | 10^{-5} | 10^{-6} | — |
| Sensitive CdS (Contains deliberately incorporated impurities such as Cl and Cu) | 10^{-1} | 10^{-2} | 10 |
| Experimental Sensitive CdS (Contains only traces of iodine impurity) | 10^{-1} | 10^{-2} | 10^{-1} |

*Also the response time for very high light level excitation.

experimental sensitive cadmium sulfide crystals with the standard sensitive crystals containing chloride and copper impurities. The immediate problem is to consolidate these advances made with single crystals and to determine whether they can be successfully carried over to other forms of photoconductors, such as powders and sintered layers. In addition, there are certainly many uses of photoconductors which do not require the limits of gain and speed to be pushed so intensely, so that a rapid growth in applications and developments over the next few years can be anticipated.

REFERENCES

1. For a more complete description of photoconductors and photoconductivity, see R. H. Bube, *Photoconductivity of Solids*, John Wiley & Sons (In Press).
2. A. Rose, RCA Rev. 12, 362 (1951); Phys. Rev. 97, 322 (1955); Proc. I.R.E. 43, 1850 (1955).
3. R. H. Bube, Proc., I.R.E. 43, 1836 (1955); J. Phys. Chem. Solids 1, 234 (1957).
4. A. Rose and M. A. Lampert, RCA Rev. 20, 57 (1959); Phys. Rev. 113, 1227 (1959).
5. R. W. Smith, RCA Rev. 20, 69 (1959).
6. H. B. Devore, RCA Rev. 20, 79 (1959).
7. R. H. Bube and L. A. Barton, RCA Rev., December 1959.

DR. RICHARD H. BUBE received the Sc.B. degree from Brown University in 1946 and the Ph.D. degree in Physics from Princeton University in 1950. Since 1948 he has been associated with RCA Laboratories Division at Princeton, N. J., currently in the Physical and Chemical Research Laboratory, where he has been engaged primarily in research on luminescence and photoconductivity of solids. Dr. Bube is a Fellow of the American Physical Society, and a Member of Sigma Xi and The American Scientific Affiliation. (See photo P. 28.)



SOLID STATE ANALOG OF THE VACUUM TRIODE



DR. W. RUPPEL

*Physical and Chemical Research
Laboratories RCA Ltd.
Zurich, Switzerland*

and

R. W. SMITH

*Physical and Chemical Research
RCA Laboratories
Princeton, N. J.*

SPACE-CHARGE-LIMITED currents in vacuum tubes have, for a long time, been a familiar subject for engineers and physicists. The current in a vacuum tube is carried by electrons that are injected from the hot cathode into the vacuum. The injected electrons form a cloud of negative space charge in front of the cathode. This space charge prevents more electrons from leaving the cathode and this limits the current. Fig. 1 shows the potential distribution between cathode and anode in the vacuum tube; the curvature of the potential distribution indicates the presence of negative space charge.

THE INSULATOR AS VACUUM ANALOG

In a solid-state analog of the vacuum triode the vacuum is replaced by an insulator. Electrically, an insulator is indeed very similar to a vacuum, since

it also represents a space devoid of free charge carriers. In the same way that electrons are injected from a thermionic cathode into vacuum, they are injected from a properly designed cathode into the *electrical vacuum* of an insulator. In like manner, holes could be injected from the anode into the insulator. In this paper, we are concerned only with electron injection. Fig. 2 shows the resulting potential distribution in the insulator. The electrons are "shot through" the insulator from the cathode to the anode. Provided that electrons can readily enter the insulator the current will only be limited by the space charge that is formed by the electrons in the insulator. The magnitude of the space charge is like that in a vacuum diode, given simply by the product of the applied voltage and approximately the interelectrode capacitance. The space charge prevents further excess electrons from entering the insulator by simple electrostatic repulsion, in the same way as the electron space-charge cloud before the cathode in the vacuum tube limits the anode-current flow.

While the principles of space-charge-limited current injection into vacuum

and into an insulator are the same, the experimental conditions for achieving space-charge-limited current flow are different in both cases.

First, concerning the electron emitting contact, in both cases it is principally desirable to have an electron reservoir in the cathode from which electrons can freely enter the vacuum or the insulator. In order to obtain an appreciable electron emission current into vacuum, it is necessary to bring the electron emitting thermionic cathode to a high temperature. In contrast, free-charge carriers can be injected into an insulator already at room temperature. A contact that provides such a reservoir of carriers is called an *ohmic contact*. On the other hand, if the free charge carriers in the contact material have too low an energy to be able to enter the insulator, the contact is called *blocking*, since it blocks the current flow. If one ohmic and one blocking contact are applied to an insulator, carriers can only be injected in one direction, and the arrangement is a rectifier. In the same way, the familiar vacuum diode can be looked upon as a vacuum space to which one ohmic and one blocking contact are made.



DR. WOLFGANG RUPPEL attended the University of Karlsruhe from 1947 to 1951 and the University of Grenoble from 1951 to 1952. He received his doctor's degree from Braunschweig in 1955. Dr. Ruppel joined RCA Laboratories in Zurich in 1955 and since then has worked on the physics of Electrofax and insulators.



ROLAND W. SMITH received the B.S. degree from Western Kentucky State College in 1939, and the M.S. degree in Physics from Northwestern University in 1942. From 1942 to 1947 he did research for the Office of Scientific Research and Development. In 1947 he joined RCA Laboratories Division at Princeton, N. J. and since then has worked on insulators. Mr. Smith is a member of the American Physical Society and Sigma Xi.

Second, the crystal lattice of the insulator and its various defects bring in alterations from the well-known space-charge-limited current flow in vacuum. In a vacuum tube, the electrons will, in general, be able to reach the anode without collision with a residual gas ion. In other words, the mean free path of the electrons is of the order of the tube dimensions. In an insulator, the electrons are scattered mainly by thermal vibrations of the crystal lattice. This effect causes the mean free path of the conduction electrons in the insulator to be 1 to 100 interatomic distances. For this reason, space-charge-limited currents in an insulator of the dimensions of a vacuum tube will be extremely small, but they can become very pronounced at electrode distances below, say, 1 mm.

Further, in vacuum the electron is accelerated by an electric field, like a freely falling body is accelerated by the gravitational field. In a solid, the electrons move with constant velocity due to "friction" with the crystal lattice, like a body falling with constant velocity through a viscous liquid.

Finally, while all electrons in a vacuum tube are free to move, the electrons in an insulator while travelling from the cathode to the anode are

trapped by lattice defects or impurity atoms during a large fraction of their transit time. This causes a reduction of the current, since an electron contributes to the electrical current only while it is free. In most of the insulating materials used in common insulator technology, such as ceramics, high-polymer organics etc., space-charge-limited injection currents are not observed because of the highly imperfect crystal structure of these materials. The imperfections give rise to excessive trapping and a consequent suppression of the injection current.

For the observation of space-charge-limited currents, crystals of a very high degree of perfection are required. It is a paradox that a perfect insulator crystal is the best insulator when injection is prevented but that it can carry the largest currents when there is injection from an ohmic cathode. It then becomes "translucent" to electrons.

SOLID-STATE TRIODES

We have seen that by applying one ohmic and one blocking contact to an insulator, the solid-state analog of the vacuum diode is obtained. To make an analog triode, one has to apply a "grid" by which the space-charge-limited cur-

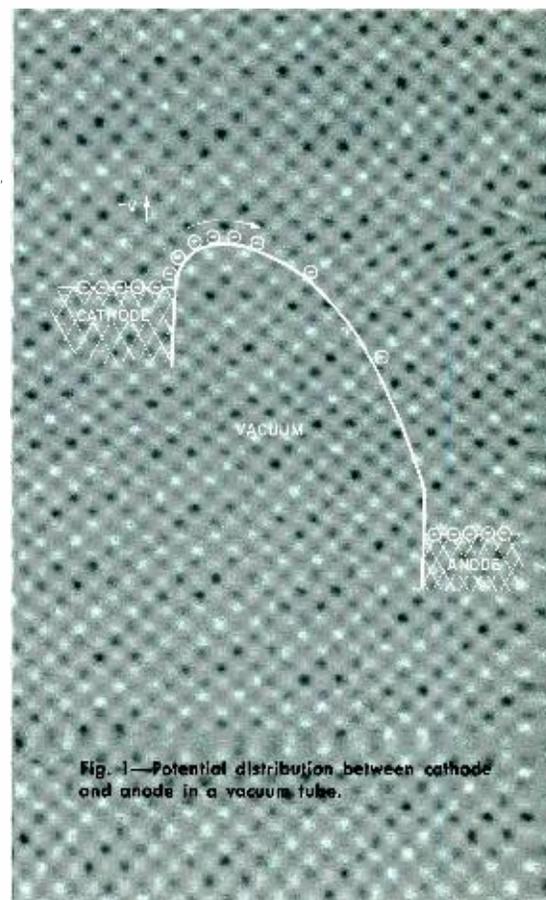


Fig. 1—Potential distribution between cathode and anode in a vacuum tube.

rent is modulated. Since it is desirable that there be no grid current, the grid should form a blocking contact to the insulator.

At this point, it might be timely to outline briefly the difference between an analog triode and the various forms of transistors in use. In none of the actual transistors is use made of the modulation of a space-charge-limited excess carrier injection current. A *p-n* semiconductor structure making use of space-charge-limited currents and termed the *analog transistor* was proposed some years ago by Shockley, but apparently has not been built. The common transistor is a *bipolar* device, i.e. the motion of carriers of both signs, electrons and holes, is involved in its operation. Bipolar transistor action implies the injection of minority carriers into a semiconductor in which space-charge neutrality is maintained. In the *unipolar* transistor, the motion of carriers of only one sign is relevant for the operation of the device, but no excess carrier injection takes place. Rather, the control electrode acts to deplete the already existing thermal equilibrium density of carriers. Hence the electron current flow in the space between cathode and grid (or, in the case of a *p*-type semiconductor, the hole

Fig. 3—CdS analog triode with a common pin head for size comparison.

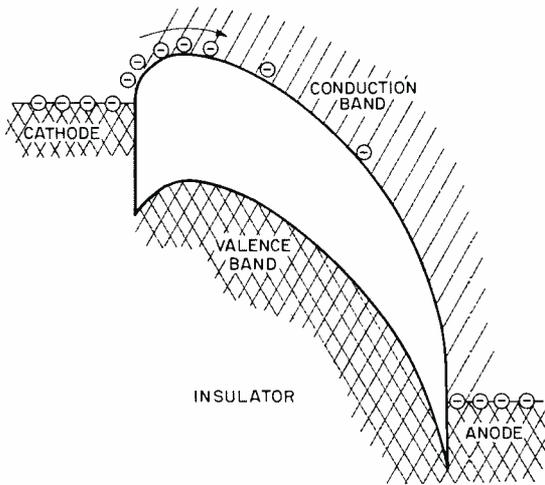


Fig. 2—Potential distribution between cathode and anode in an insulator with an ohmic cathode.

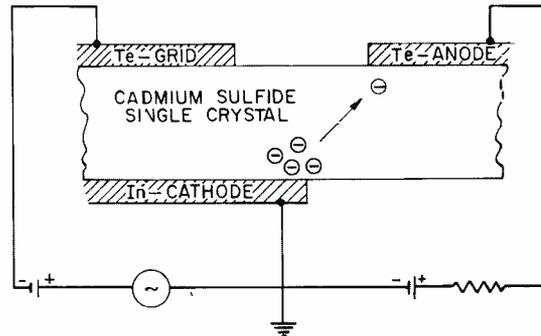


Fig. 4—Cross section through insulator analog triode

current flow between anode and grid) is not space-charge-limited.

THE ANALOG TRIODE

The actual construction of an insulator analog triode in which a space-charge-limited current is modulated in close analogy to a vacuum triode has become possible since Smith and Rose discovered some years ago in the RCA Laboratories that large space-charge-limited currents can be drawn through insulating cadmium sulfide single crystals.

A cadmium sulfide analog triode which demonstrates the principle of analog operation is shown in Fig. 3. Fig. 4 shows the cross section through the essential part of the device. The insulator substituting for the vacuum is a cadmium sulfide single crystal, about 1/100 mm thick. The electron-emitting cathode is formed by evaporated indium metal, and the blocking grid electrode consists of evaporated tellurium. The work function of the anode material is of no more importance for the performance of the analog triode than it is for the vacuum triode. For the convenience of application, it is also made from tellurium.

Since the device operates in a way analogous to the vacuum triode, its circuit connections are similar. The basic

circuit elements are indicated in Fig. 4. A space-charge-limited current is drawn between the cathode and the anode. If the grid is biased negatively, its negative potential extends into the cathode-anode space. The negative charge on the grid can be considered as enhancing the negative space-charge between cathode and anode. Since this charge is a bound charge, it does not contribute free carriers to the current flow, but rather acts to enhance the space-charge barrier, thus reducing the anode current.

By space-charge-limited carrier injection into a cadmium sulfide single crystal, a current flows that is more than a million times higher than the current through the crystal without excess carrier injection from the contact. This current is reduced to a small fraction of its initial value by the application of a few volts to the grid electrode. The current drawn from the grid is extremely small, so that the device becomes a high-impedance amplifier. The frequency response of present devices extends from d-c over the audio-frequency range.

SUMMARY

Space-charge-limited current through insulators can be modulated in a way

analogous to those in a vacuum triode. Mainly because the mean free path of a charge carrier in a solid is much shorter than in vacuum, space-charge-limited currents are likely to be realized only at very small interelectrode distances. For this reason, an analog triode is a very small device, and the principle of analog operation is well suited for the development of integrated devices. The frequency response of present preliminary forms of the device is limited to the audio range. This limitation is probably due to trapping processes, and any improvement in the preparation of pure insulating single crystals is expected to shift this limitation to higher frequency values. The high input impedance of the grid electrode allows the analog triode to fit a number of applications not accessible to commercial transistors.

While preserving all the essential features of the corresponding vacuum devices, the solid-state analog devices will have a greater versatility of applications by virtue of the well-known advantages of a solid-state device, such as small size, absence of a heated cathode, long life time, low cost, rigid construction, reliability, and possibility of high-temperature operation.

DIELECTRIC CERAMICS IN ELECTRON TUBES

by

W. J. KOCH and T. F. BERRY

Chemical and Physical Laboratory

Electron Tube Division

Harrison, New Jersey

THE WORD CERAMIC is derived from the Greek word *keramos*, meaning "a potter," "potter's clay," or "pottery," and is related to an older Sanskrit root meaning "to burn." The definition generally given for a ceramic is "a product obtained through the action of fire upon an earthy material." This all-inclusive definition covers not only electrical and thermal insulators, but also structural products, such as refractories and building materials, glass, enameled ware, abrasives, and cements. The special and specific types of ceramic insulating materials used in electron tubes, however, have brought a new meaning to this definition.

Ceramic dielectric materials are used in electron tubes primarily as external and internal insulators; e.g., as electrode spacers in power tubes, or as the tube envelope of the Nuvistor tetrode and power tube. These ceramic parts must be very pure and have a known and fixed chemical composition in order to permit a high degree of electrical performance and to prevent tube contamination.

The ever-increasing demand for ceramics having better dielectric properties has led to new techniques in the processing of these materials. Such techniques include the use of very pure raw materials, better pressing and firing methods, phase-diagram investigations, X-ray analyses and various types of microscopic inspection.

The first insulators were made from mixtures of various clays, feldspar, and silica, all of which are mined from the earth. Although washed and graded, they contained varying amounts of trace impurities. Raw materials presently used in the manufacture of ceramics for electron tubes are either chemically pure, precipitated compounds, or natural materials which have been refined and purified so as to keep the trace impurities at a fixed and low level.

CERAMICS USED IN ELECTRON TUBE INDUSTRY

The principal ceramic dielectric materials used in the Electron Tube Division occur in the magnesia-alumina-silica system, a phase diagram of which is shown in Fig. 1.¹ Suitable proportions of these *end members* (single oxides of the phase system) mixed in varying

quantities and fired to the proper temperatures produce ceramic articles no longer composed of a mixture of the various end members, but rather a completely new crystalline compound having superior electrical properties. If, in the case of the magnesia-alumina-silica system, the body composition is compounded so as to produce a microcrystalline structure in which the primary crystalline phase is forsterite ($2\text{MgO}\cdot\text{SiO}_2$), the resultant ceramic body is called a *forsterite* body. If, on the other hand, the magnesia content is reduced and silica content is correspondingly increased, the primary crystalline phase will be protoenstatite ($\text{MgO}\cdot\text{SiO}_2$) rather than forsterite, and the resultant body is then called *steatite*. Because compounds of this type are formed by partial melting and subsequent recrystallization, the resultant ceramics are likely to contain varying amounts of glass which has not completely crystallized.

Ceramics having a composition which is predominantly that of an end member are generally referred to by the name of the primary crystalline phase, as, for example, magnesia. Theoretically, such ceramics should contain no glass. Because such compounds are generally very refractory, the manufacturer adds fluxes which permit firing at lower temperatures. This practice, unfortunately, tends to form glass and, as will be demonstrated, glass has a significant effect on the physical and electrical properties of the ceramic.

Because each vendor has developed a particular material formulation and fabrication procedure, the "same" ceramic purchased from different vendors may have only reasonably similar electrical and physical properties, and even these may vary from shipment to shipment.

STRUCTURAL DETERMINATIONS

Both X-ray and microscopic inspection techniques are helpful in maintaining the desired compound uniformity. X-ray analyses can quickly and readily reveal the presence of deleterious secondary phases, but only if these phases are present in amounts greater than 5 to 10 percent. However, X-ray analyses yield no information concerning glass or porosity of a ceramic body.

Microscopic techniques are particu-

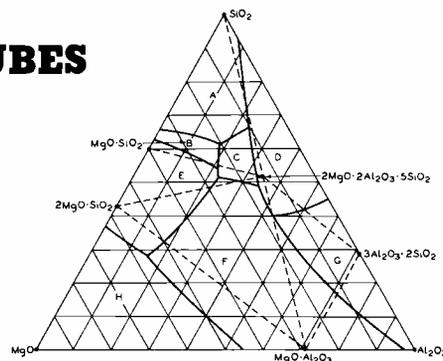


Fig. 1—Phase diagram, $\text{MgO}\text{-Al}_2\text{O}_3\text{-SiO}_2$. A, quartz; B, enstatite; C, cordierite; D, mullite; E, forsterite; F, spinel; G, corundum; H, periclase.

larly well suited for the determination of structures or flaws which influence the finished device. The traditional microscopic methods consist of examination of crushed fragments or specially prepared, ground, thin sections of the ceramic material in the transmitted light, followed by subsequent determination of the minerals present in the fired product. The crushed-fragment method gives no structural information, and the thin-section method is not only tedious and laborious, but is limited to non-opaque minerals. More recently, the polished section technique has come to the fore.² This method is quite rapid; is applicable to metal-ceramic brazed structures; and is quite capable of revealing such internal structures of the ceramic as pores, crystal phases and sizes, and the amount of glass present. Such structures can and do affect such physical properties of the ceramic as strength, thermal conductivity, thermal expansion, electrical resistivity, power factor, dielectric constant, and other electrical properties. For example,^{3,4} the shape and number of pores in a given ceramic can alter the thermal conductivity by a factor of 10, and the presence and the type of glass in a steatite composition can result in a change in loss factor from 0.016 to 0.004.

To illustrate the use of polished sections, as well as to acquaint the reader with microstructural differences between various vendor's electronic ceramics, a series of photomicrographs have been prepared. Fig. 2 shows a weak forsterite ceramic which resulted in poor seals. Improvements in processing by the vendor resulted in the stronger, more homogeneous structure shown in Fig. 3. In each Figure, the black, roughly circular areas are pores. It is apparent that the latter shipment (Fig. 3) is denser than the earlier one. Fig. 4 is a photomicrograph of the same body shown in Fig. 3, but made at a higher magnification to show the crystalline nature of the ceramic more clearly. The forsterite crys-

tals are observed to be light gray in color and approximately hexagonal in outline. The lighter gray material between the crystals is the residual glass. Again, the dark areas are the pores. Fig. 5 shows another forsterite ceramic, made by a different manufacturer, having much smaller forsterite crystals and different glass distribution. Such microstructural variations are the result of different batch compositions, as well as processing methods, and are a valuable clue to the properties of the respective materials.

Microscopic evaluation can also be used to "trouble-shoot" or monitor processes in which the ceramics are used. Figure 6 shows a forsterite body prior to metalizing and Fig. 7 shows the same body heated to too high a temperature during a metalizing process. The increase in the size of the pores is a definite indication that the body has been overfired. A decrease in the temperature of the metallizing process permitted successful metallization of this particular ceramic.

FORSTERITE CERAMICS

A ceramic widely used for small ceramic-metal assemblies (one inch in diameter or less) in the tube industry is forsterite. It has a softening temperature approximately 100°C higher than that of steatite and, in addition, has a thermal expansion similar to that of the nickel steel used in vacuum-tube envelopes. The thermal expansion character-

TABLE I—INSULATING MATERIALS, CERAMIC RADIO CLASS L, JAN-I-10

| Properties | Requirements | | | | | |
|------------------------------------|--|-------|-------|---------------|-------|-------|
| Porosity | No penetration of liquid under 10,000 psi pressure | | | | | |
| Flexural Strength | Not less than 3,000 psi | | | | | |
| Resistance to thermal change | | | | | | |
| Grade | A 20 cycles | | | B 5 cycles | | |
| Requirements | Boiling water to ice water | | | | | |
| Dielectric strength | Not less than 180 rms volts per mil | | | | | |
| Loss Factor | (Power factor times Dielectric constant) | | | | | |
| Grade | L-1 | L-2 | L-3 | L-4 | L-5 | L-6 |
| Loss Factor (max.) | 0.150 | 0.070 | 0.035 | 0.016 | 0.008 | 0.004 |
| Dielectric Constant ... | Not over 12 after immersion in water for 48 hours | | | | | |

istics of several ceramic materials are shown in Fig. 14.⁵ The close similarity of forsterite to this metal in linear coefficient of thermal expansion throughout the temperature range from 25 to 800°C makes it possible to obtain good strain-free vacuum-tight seals even after extremes in thermal cycles in processing or service. Forsterite ceramics have excellent electrical properties, as seen in Table I, but have relatively low thermal-shock resistance, due primarily to their high coefficient of linear thermal expansion. Forsterite ($2\text{MgO}\cdot\text{SiO}_2$), like steatite ($\text{MgO}\cdot\text{SiO}_2$), is generally compounded from talc ($3\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$), an inexpensive source of MgO with good fabricating properties. Talc contains sufficient MgO to form protoenstatite, but for a forsterite composi-

tion, the ceramic engineer must add additional magnesium oxide, as well as suitable alkaline earth oxides to obtain the fired properties associated with a ceramic structure whose principal crystalline phase is forsterite.

Because of the nature of the raw materials used in the production of forsterite, control of the final parts dimensions has been rather difficult in the past. However, new processing techniques developed at the Harrison Chemical and Physical Laboratory now permit the production of low-cost, close-tolerance forsterite parts.

The physical properties of an average forsterite ceramic composition used in electron tubes are shown in Table II. (The microstructures of forsterite have been illustrated previously.)

TABLE II—TYPICAL PHYSICAL PROPERTIES OF CERAMIC DIELECTRICS (VITRIFIED CERAMICS)

| | Steatite | Forsterite | Zircon | Alumina |
|--|--------------------------------------|---------------------------------|--------------------------------------|--------------------------------------|
| Specific Gravity, g/cc | 2.5-2.7 | 2.7-2.9 | 3.5-3.8 | 3.1-3.9 |
| Water Absorption, percent | 0.00 | 0.00 | 0.00 to 0.01 | 12 to 0.00 |
| Safe Operating Limit, °C..... | 1000-1100 | 1150-1250 | 1000-1200 | 1350-1500 |
| Thermal Expansion-Coefficient Per °C, (25 to 700°C), inch/inch | $7.0 \text{ to } 9.0 \times 10^{-6}$ | 10.5×10^{-6} | $3.5 \text{ to } 5.5 \times 10^{-6}$ | $5.8 \text{ to } 8.1 \times 10^{-6}$ |
| Thermal Shock Resistance | Moderate | Low | Good | Excellent |
| Tensile Strength, psi | 8,000-20,000 | 8000-10,000 | 10,000-15,000 | 8000-30,000 |
| Compressive Strength, psi | 65,000-130,000 | 60,000-100,000 | 80,000-150,000 | 80,000-250,000 |
| Flexural Strength, psi | 16,000-24,000 | 18,000-27,000 | 20,000-35,000 | 40,000-60,000 |
| Thermal Conductivity, watts-cm ⁻² -cm-°C ⁻¹ | 0.021-0.025 | 0.021-0.042 | 0.042-0.063 | 0.05-0.25 |
| Modulus of Elasticity, psi | $13 \text{ to } 15 \times 10^6$ | $13 \text{ to } 15 \times 10^6$ | $20 \text{ to } 30 \times 10^6$ | $15 \text{ to } 52 \times 10^6$ |
| Dielectric Strength for ¼-inch-thick specimen, volts/mil | 200-350 | 200-300 | 250-300 | 250-400 |
| Power Factor at 1 Mc | 0.0008-0.0035 | 0.0003 | 0.0006-0.0020 | 0.001-0.002 |
| Dielectric Constant | 5.5-7.0 | 6.2 | 8.0-9.0 | 8.0-9.0 |
| Resistivity at 25°C, ohm/cm ³ | 10^{13} - 10^{15} | 10^{13} - 10^{15} | 10^{13} - 10^{15} | 10^{14} - 10^{15} |
| L-Grade (JAN Spec. I-10) | L-3 to L-6 | L-6 | L-4 | L-2 to L-5 |

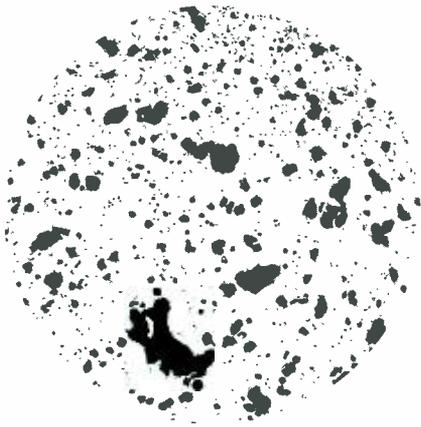


Fig. 2—Forsterite (A), 1956 shipment (100x)

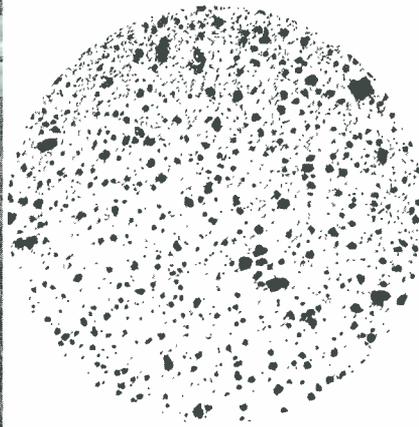


Fig. 3—Forsterite (A), 1958 shipment (100x)

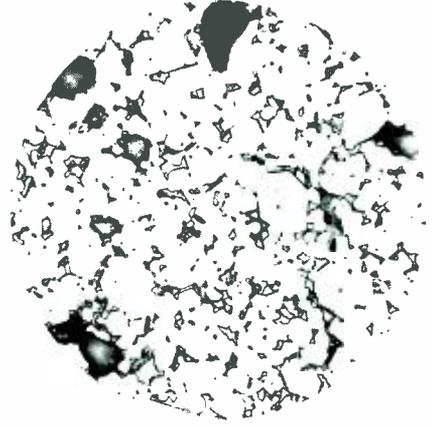


Fig. 4—Forsterite (A), 1958 shipment (750x)

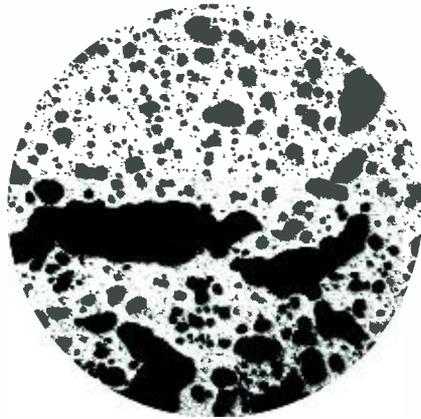


Fig. 5—Forsterite (B), (750x)

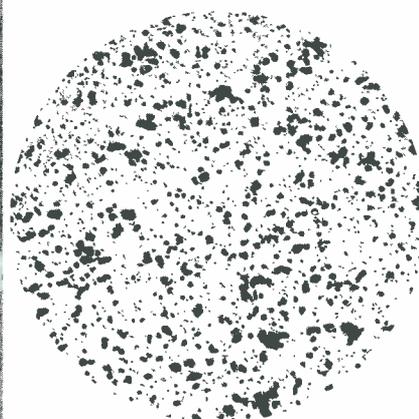


Fig. 6—Forsterite (C), (100x), prior to metalizing

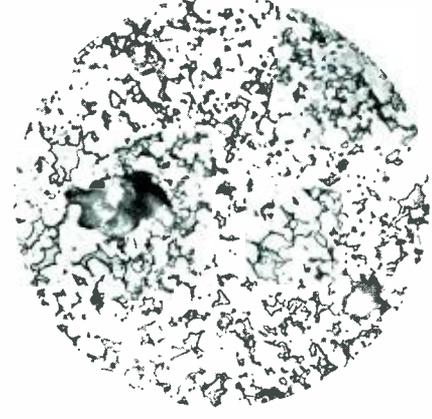


Fig. 7—Forsterite (C), (100x), heated to too-high temperature during metalizing.



Fig. 8—Steatite, (100x)

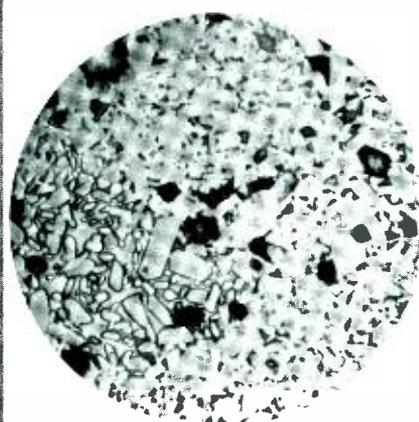


Fig. 9—Alumina (A), (750x)

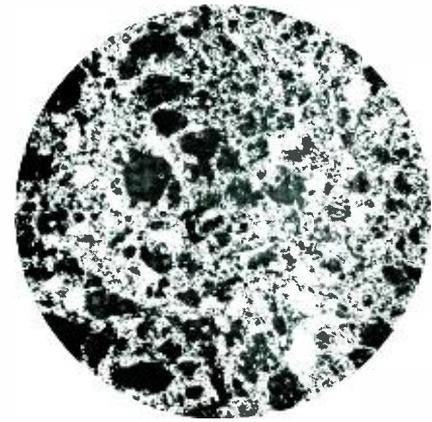


Fig. 10—Alumina (B), (750x)

STEATITE CERAMICS

Steatite is widely used as a high-frequency ceramic insulating material, and is made in various electrical grades. In general, an L-4 body (Mil Spec JAN-I-10, shown in Table I) contains the minimum electrical and mechanical requirements necessary for tube parts. The chief raw material used in the manufacture of steatite is a very-high-purity grade of talc. Unlike other ceramic raw material, talc is very soft and, therefore, more-intricate parts can be pressed and mass produced from steatite than from harder material. Moreover, talc does not abrade the hardened steel or tungsten carbide tools used in the extrusion or dry-pressing of the unfired or green parts. As a result, such parts can be held to very close dimensional tolerances. In addition, steatite requires a relatively low firing temperature (1250 to 1325°C), depending upon specific composition, to achieve vitrification and maximum fired density. Consequently, the cost of steatite parts is lower than that of other dielectric ceramic parts of the same design.

The chief limitations of steatite are the relatively high linear coefficient of thermal expansion, its relatively low strength, and its comparatively low softening temperature. High thermal expansion and moderate strength cause steatite parts to have poor thermal-shock resistance. Such properties can be directly related to the microstructure of steatite, which is illustrated in Fig. 8. The light gray protoenstatite crystals are almost completely surrounded by a darker gray glass matrix. Because of thermal expansion mismatch between the crystalline and glass phases, ceramics having this type of structure frequently have poor thermal-shock resistance.

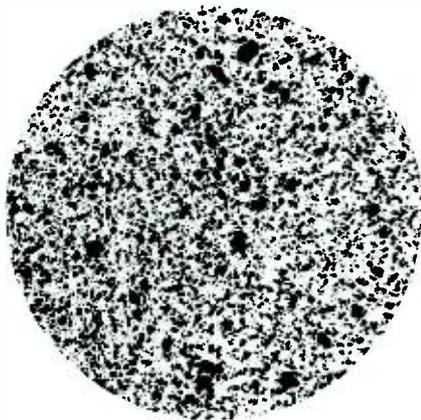


Fig. 11—Beryllia, (100x)

ALUMINA CERAMICS

Alumina ceramics, despite their higher cost are finding wide application in all phases of electronic ceramics. Although alumina exhibits lower thermal expansion than metals, the high strength of this material permits the use of alumina ceramic parts in electron tubes without danger of cracking at the metal-to-ceramic bond during thermal cycling. Table II, for example, shows that alumina has a flexural and impact strength about three times that of steatite.

Another advantage of the use of this material in electron tubes is its relatively high thermal conductivity, as compared to other dielectric ceramics. Comparative thermal conductivities are shown in Fig. 13.⁶ Because alumina is very abrasive (second to diamond on the Mohs scale of hardness) alumina ceramics are higher in cost than the other dielectric ceramic materials in general use as electronic ceramic parts. More-expensive carbide tools, rather than hardened-steel tools, must be used to press or extrude the green, or unfired, material.

Alumina forms into the proper microcrystal structure only after considerable heat work has been done to it, so that firing temperatures between 1500 to 1750°C (depending on the specific alumina body composition) are required to obtain a dense, high-strength, vacuum-tight part. In general, the longer firing times, higher fuel costs, and more expensive furnaces and setting materials required for the fabrication of alumina dielectric parts, all contribute to a higher unit price.

Alumina is a very stable oxide and has excellent resistance to reducing atmospheres. The high refractoriness of alumina permits electron-tube parts to be metalized, brazed, and outgassed at high temperatures resulting in cleaner, lower-

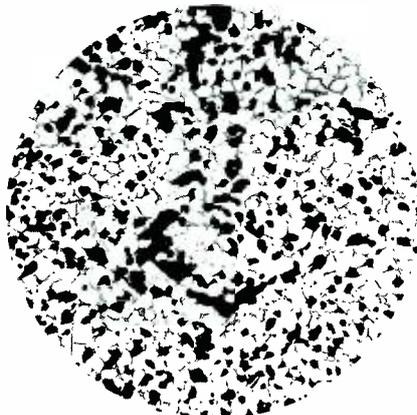


Fig. 12—Zircon, (100x)

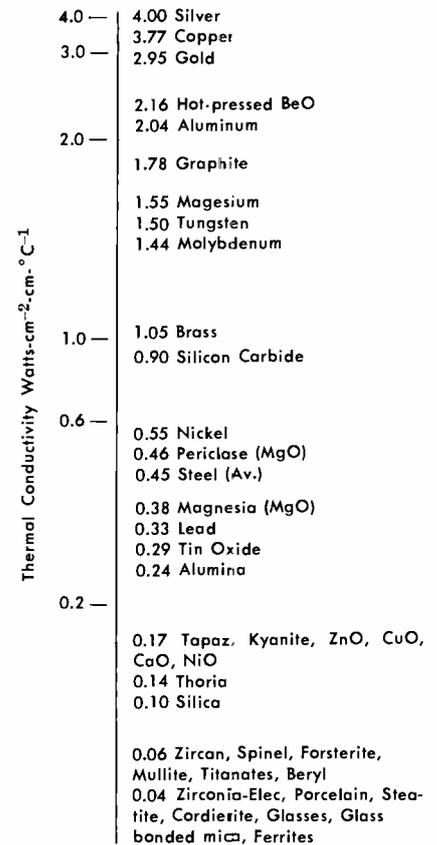


Fig. 13—Thermal conductivity of some common metals and ceramics used in vacuum tubes.

gas-level tubes. Some porous alumina bodies are used for special parts, such as grid spacers and supports, in which refractoriness and ease of outgassing are most desirable.

Figs. 9 and 10 illustrate the variations in microstructure which are observable in commercial alumina ceramics from different suppliers. Although both bodies contain approximately 95 percent of alumina, the difference in crystal size between the two bodies is quite pronounced. This illustration again should serve as a reminder to design engineers that similarity in chemical composition does not necessarily guarantee similar physical or electrical ceramic properties. In both Figures, the alumina crystals are the light gray hexagonal areas, and the interstitial darker gray patches are glass between the crystals.

BERYLLIA CERAMICS

Beryllia ceramics have thermal conductivity equal to that of aluminum metal. This material also has good dielectric properties and is very refractory. Beryllia, however, is so highly toxic, particularly during the parts preparation and firing stages, that the capital investment needed to produce this material safely is high. In addition, like alumina, fabrication costs are high. This combined with the limited quantities of the raw

material cause the unit price of beryllia ceramics to be prohibitive for most electron-tube applications. The microstructure of beryllia is illustrated in Fig. 11. Like alumina, this ceramic is predominantly crystalline with only a small amount of darker gray interstitial glass. In these structures, the physical and electrical properties are largely determined by the predominant crystalline phase.

ZIRCON CERAMICS

Another dielectric ceramic material used in electron tubes is zircon porcelain. The principal crystalline phase of this ceramic is zircon ($ZrO \cdot SiO_2$), which is mixed with clay and other fluxes to promote vitrification. Fired zircon ceramic bodies (Table II) have good mechanical strength and the dielectric properties are fair to good. Zircon bodies are generally rated as Grade L-4 dielectrics, because mined, rather than chemically prepared and generally less pure, raw materials are used to fabricate this type of ceramic. The outstanding characteristic of this material is its low coefficient of thermal expansion. If a ceramic body has a low thermal expansion coefficient, it does not become strained severely during thermal cycling and, therefore, has good heat-shock characteristics. The high strength of zircon also aids considerably in realizing good thermal-shock resistance. Zircon dielectric bodies metalize very well. They can be fabricated by the standard ceramic techniques of dry pressing and extruding, but, because zircon is quite abrasive, more expensive tungsten carbide rather than hardened steel tools are required. The price of pieces made from this material is higher than that of steatite but less than that of forsterite and alumina prices. Due to its relatively high impurity level and, in general, lesser physical and electrical properties, this material has been gradually replaced by alumina ceramics for use in electron tubes.

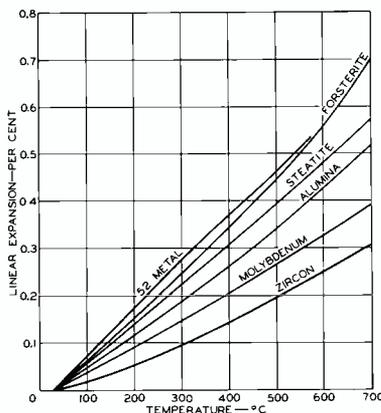


Fig. 14—Thermal expansion of some common metals and ceramics used in vacuum tubes.



THOMAS F. BERRY (left) studied ceramics both at Columbia University in New York City and at Rutgers in New Brunswick, N. J. 1940 to 1956 he was employed at the Fundamental Research Laboratory of U. S. Steel in Kearney, New Jersey, progressing from his initial work as a laboratory technician through the jobs of experimental machinist and assistant petrographer to the position of associate physicist. He joined the Chemical and Physical Laboratory of the Electron Tube Division in Harrison in 1956 and has been concerned with investigating fundamental factors controlling fired dimensions of ceramics, establishing techniques for metalizing ceramics, and developing microscopic techniques for evaluation of ceramic-tube metal seals. Mr. Berry has co-authored several papers in the field of ceramics and holds two patents in this field. He is a member of the American Ceramic Society, the American Institute of Metal Engineers, and The American Society for Metals.

The microstructure of a zircon ceramic, shown in Fig. 12, is somewhat similar to that of steatite in that the zircon crystals are almost completely surrounded by a glass matrix. Its excellent thermal-shock resistance as compared to steatite is due to the very low and nearly equal thermal expansion characteristics of the crystalline and glass phases.

SUMMARY

The basic dielectric ceramic materials have been generally available for the past ten to fifteen years. The early dielectric ceramics were made from rather impure raw materials, but continually increasing demands for better dielectric properties and extremely close dimensional tolerances required the ceramic engineer to develop new concepts of body composition and preparation by the use of pure materials and process controls. In addition to the use of pure chemically prepared raw materials, fabrication techniques have been completely changed to include spray drying which results in a free-flowing, uncontaminated powder, of uniform granule density suitable for easier dry-pressing. New and better firing and testing have also contributed to the improvement.

Relatively low-cost dielectric ceramics having extremely close dimensional tolerances are currently being made at Harrison. Such results stem largely from work done in the Harrison Chemical and Physical Laboratory which indicates that linear dimensional shrinkage is largely influenced by the density of the granule from which the parts are pressed.^{7,8} Other parameters such as

WILLIAM J. KOCH (right) received a B.S. in 1943 and an M.S. degree in ceramics in 1947, both from Rutgers University. He did further graduate work toward a Ph.D. degree at Ohio State University during 1948 and 1949. From 1943 to 1946, he served as a 2/Lt., USAF, working on the Army Airways Communications System. From 1947 to 1951, he worked at Battelle Memorial Institute in Columbus, Ohio as engineer in charge of white-wear ceramics research projects. From 1951 to 1953, he was Senior Project Engineer in charge of ceramics for the National Bureau of Standards of the U. S. Navy project "Tinkertoy." In 1953, he became Technical Director of ceramics for P. R. Mallory and Co. where he designed and directed a plant for the manufacture of titanate ceramic capacitors. In 1956, he designed and installed a small dielectric ceramic plant to fabricate steatite parts for ACF Electronics in their electronic module fabricating facility. He joined the Chemical and Physical Laboratory of the Electron Tube Division in Harrison in 1958, and is currently working on the Nuvisor program. Mr. Koch is the author of several technical papers and has been granted several patents in the field of ceramics. He is a Professional Engineer, a member of the American Ceramic Society, and a member of the Institute of Ceramic Engineers.

pressed or unfired density, ignition loss, and fired density, and their inter-relationship have been determined and are being accurately controlled. In all of this work, the use of the reflected-light microscope has aided considerably in obtaining basic information regarding body structure, crystalline and glass phases, as well as internal porosity of dielectric ceramics.

BIBLIOGRAPHY

1. Phase Diagrams for Ceramists, J. Amer. Ceram. Soc., 1947, p. 142, Fig. 379.
2. Examination of Refractory Specimens in Reflected Light, R. B. Snow, J. Amer. Ceram. Soc., Vol. 36, No. 9, p. 299, 1953.
3. Thermal Stress Resistance of Ceramic Materials, W. D. Kingery, J. Amer. Ceram. Soc., Vol. 38, p. 11, 1955.
4. Effect of Porosity on Physical Properties of Sintered Alumina, R. L. Coble and W. D. Kingery, J. Amer. Ceram. Soc., pp. 377-385, 1956 39 (11).
5. Thermal Properties of Ceramics, E. J. Smoke, and J. H. Koenig, Engineering Research Bulletin #40, Rutgers University, Jan. 1958.
6. Thermal Conductivity, Special Issue, J. Amer. Ceram. Soc., Vol. 37, No. 2, Feb., 1954, Part II.
7. Role of Powder Density in Dry-Pressed Ceramic Parts, T. F. Berry, W. C. Allen, and W. A. Hassett, Amer. Ceram. Soc. Bull., Vol. 38, No. 8, p. 393, Aug. 1959.
8. Stoichiometry of Ceramic Dimensional Control, W. C. Allen, Electron Tube Division RCA Presented Annual Meeting, Amer. Ceram. Soc., May, 1959, to be published in J. Amer. Ceram. Soc. in 1960.

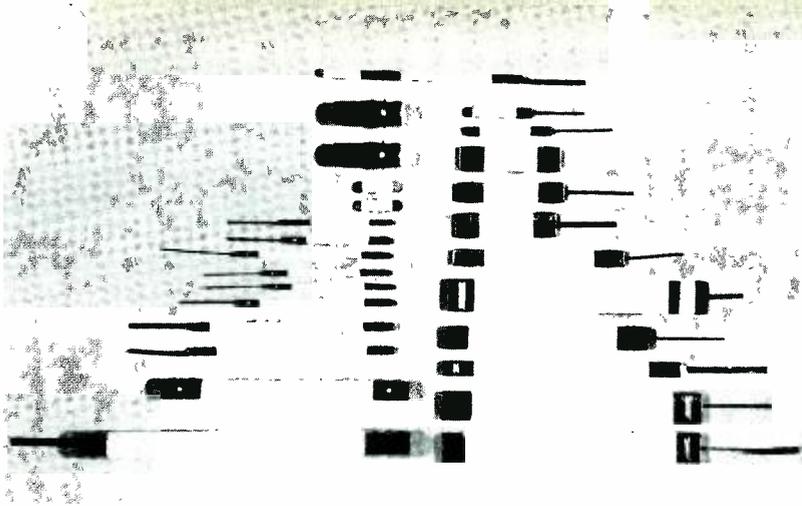


Fig. 1—Typical oxide-coated cathodes used in electron tubes. The metal tabs provide electrical connection from the cathode to the stem leads.

A NEW APPROACH TO THE CONTROL OF CATHODE ALLOYS

by

DR. I. F. STACY and C. W. HORSTING

*Chemical and Physical Laboratory
Electron Tube Division
Harrison, N. J.*

ALTHOUGH ANY METAL will “boil off” electrons when heated to a sufficiently high temperature in a vacuum, the most efficient electron emitter known is the oxide-coated cathode. This cathode usually consists of a nickel sleeve coated with the oxides of barium and strontium, and sometimes calcium. The cathodes in different tube types may have any of a large variety of sizes and shapes, as shown in Fig. 1.

The cathode is usually heated by means of a tungsten heater wire, which is inserted into the cathode sleeve, as shown in Fig. 2. In the temperature range from 700 to 800°C, the oxide coating on the nickel emits enough electrons to operate an electron tube.

Nickel has been chosen as the cathode sleeve material for the following reasons: (1) It is a good conductor of electricity (electrons). (2) It is a fairly good conductor of heat (helpful in maintaining a uniform cathode temperature). (3) It has a melting point well above the operating temperature of the cathode. (4) Nickel strip is easily formed into the cathode shapes needed. (5) It has a low vapor pres-

sure at operating temperature. (6) It is stable in air. (7) It is easily available and relatively low-priced.

The barium, strontium, and calcium oxides (alkaline-earth oxides) which form the emitting surface on the nickel sleeve are not stable in air. The sleeve is therefore sprayed with a mixture of alkaline-earth carbonates and a binder, usually nitrocellulose. (The binder serves only to give the coating mechanical strength so that it can withstand handling during the construction of the tube. As soon as the cathode is heated in vacuum, the binder decomposes completely into gaseous products which are pumped out of the tube.) While the air is being pumped out of the tube prior to seal-off, an electric current is applied to the heater, and the cathode is heated to break down the carbonates to the oxides and carbon dioxide as follows:



The carbon dioxide formed from the

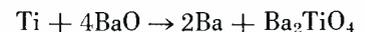
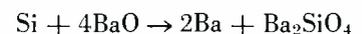
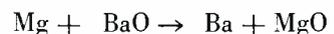
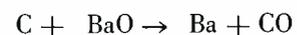
decomposition is pumped out and the tube is sealed off.

At this stage, the cathode emission is only a small fraction of what it should be in the finished tube. An additional process, known as aging or seasoning, which consists of a schedule of heating the cathode and drawing current, brings the cathode to its maximum emission capability. By means of this process, the oxide coating is partially reduced to form some uncombined barium, strontium, and calcium.

The reduction is effected by two different mechanisms. When current is drawn from the cathode, a small amount of the oxide is electrolyzed; i.e., broken down into barium, strontium, calcium, and oxygen, and the needed free alkaline-earth metals are produced. However, the electrolysis is very slow and inefficient. The second, more efficient mechanism, which operates simultaneously with the first, effects chemical reduction by means of small amounts of chemical reducing agents in the base nickel.

CATHODE BASE METAL

Among the best reducing agents used in the cathode base metal are carbon, magnesium, silicon, and titanium. They react with the coating according to the following equations (although only barium oxide is mentioned here, strontium and calcium oxides undergo similar reactions):



Each of these reducing agents, however, has an associated disadvantage. The carbon monoxide (CO) formed by the reaction with carbon can make a tube “gassy” if the carbon content of the base nickel is too high. Because magnesium has a high vapor pressure at the cathode operating temperature, the vapor may deposit on insulating surfaces and cause leakage currents. The barium silicate (Ba_2SiO_4) and barium titanate (Ba_2TiO_4) formed by the reactions of silicon and titanium, respectively, have high resistivities, so

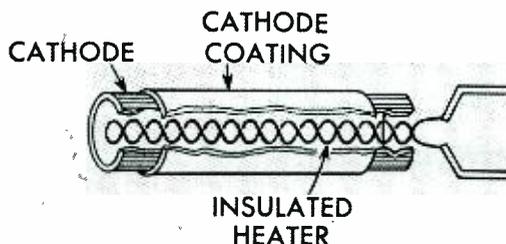


Fig. 2—Cutaway drawing of cathode showing heater, cathode sleeve, and oxide coating.

that layers of these compounds at the nickel-coating interface introduce impedances in the cathode circuit which reduce the output of the tube, especially under pulsed operation.

Each of the reducing agents must diffuse from inside the nickel to the surface before it can react with the coating. Because each diffuses at a different rate, some reducing agents are exhausted before others. Carbon, which diffuses rapidly, acts mainly during exhaust and aging. Magnesium diffuses more slowly throughout several hundred hours of life, whereas the action of silicon and titanium lasts for thousands of hours. The action of zirconium, another efficient reducing agent, is presently under investigation.

For rapid cathode activation during aging and for efficient maintenance of the reduction reaction during the full life of the tube, the cathode nickel usually contains regulated amounts of several reducing agents. The mixture of several reducing agents also serves to minimize the particular disadvantage of each. These considerations make it clear that the control of the nickel composition is of prime importance in the manufacture of electron tubes.

CONTROL OF BASE-METAL COMPOSITION

In the early days of oxide-coated cathode development, nickel for cathodes was selected solely on the basis of tube performance. In later years, when the role of reducing agents in the nickel was recognized, chemical analysis became one of the criteria for acceptance of cathode material. However, because the amount of nickel used for cathode base metal was very small compared with the amounts used in the steel industry, nickel producers would not produce special alloys for cathode nickel purposes.

With the advent of much higher standards of reproducibility and durability for military and industrial applications, it became imperative that cathode base-metal compositions be produced specifically for use in electron tubes. Custom-made alloys have been made available commercially, chiefly by two different sources: (1) A producer of cathode tubing has developed several commercially available proprietary alloys which, until recently, were all melted by conven-

tional air-melting methods. (2) RCA has developed its own alloys, utilizing the technique of vacuum-melting.

RCA began its development of vacuum-melting techniques in 1945 and produced the first commercial vacuum-melted materials in 1949 for use in directly heated cathode or filament-type tubes. It was immediately obvious that the quality of this material was superior in all respects to that produced by air melting. As a result, sleeve materials for indirectly heated cathodes were also produced. Because the volume of nickel needed for the indirectly heated cathodes was much larger than that for filamentary cathodes, a much larger installation, the 500-pound capacity furnace shown in Fig. 3 was acquired. Early in 1958, RCA began production of N132, an alloy which was designed to replace the commercially produced nickel, N109, used in the majority of RCA electron tubes. The composition specifications for N132 and for two commercially available air-melted alloys are shown in Table I.

Table I—Composition Specifications of Some Cathode Alloys
(Figures are ranges or maxima in weight percent)

| Alloy | Car- bon | Magne- sium | Man- ganese | Sili- con | Tita- nium |
|-------|----------------|----------------|----------------|--------------|---------------|
| N18 | 0.04 | 0.01- .08 | 0.20 | 0.01-.05 | 0.01-.05 |
| N109 | 0.08 | 0.03- .10 | 0.20 | 0.01-.05 | 0.005 |
| N132 | 0.015- .035 | 0.02- .04 | 0.08 | 0.01-.03 | 0.005 |

Note—N18 and N109 are selected from International Nickel Co. 220 and 330 alloys which have even wider specification limits.

An investigation of homogeneity from melt to melt and within melts not only showed the new alloy to be much more homogeneous in all respects, but also proved that the old air-melted alloys were much less homogeneous than had previously been suspected. For example, on one occasion, in an air-melted alloy, an important element like magnesium was found to vary from a concentration of 0.04 percent to 0.08 percent within a single roll of cathode strip.

These large variations, within melts as well as between melts, explained why so much difficulty was experienced with commercially available nickels. It occurred repeatedly that

melts which had been tested and approved had to be discarded, sometimes after initial successful use, because subsequent cathodes from the same melt would no longer perform adequately. With the sole exception of the alloys used in the semiconductor field, the cathode alloys which RCA is presently producing are the best composition-controlled alloys available anywhere. Even the most modern high-temperature jet-engine alloys are controlled to only tenths of a percent of minor ingredients, whereas in RCA cathode alloys, additions are controlled to within a few hundredths of a percent.

THE MELTING PROCESS

Basically, there is no secret to the reproduction of alloy melts within narrow control limits. Sufficiently pure materials must be used, and a process which does not allow the introduction of impurities must be devised. In addition, the amounts of reducing agents added and the amounts lost, as well as the melting, alloying, and rolling procedures must be very closely controlled. Material used in crucibles and crucible linings, which are in direct contact with the molten metal, must have a high degree of purity. And, of course, the alloying ingredients have to be of such purity that contamination from this source is negligible. This control is not difficult to achieve because the amounts of additives are in the order of fractions of a percent. For instance, silicon added to the melt in a concentration of 0.02 percent would cause a contamination level of only 0.0002 percent if the silicon contained as much as 1 percent of an impurity.

Because the impurity level of the main constituent is reflected directly in the composition of the resulting alloy, the purity of the nickel is of prime importance. The electrolytic nickel used has a total impurity content of 0.1 percent, of which the largest part is cobalt, an inert element in cathode nickel. All of the other impurities are present at concentrations of thousandths of a percent.

The nickel is melted in a vacuum of approximately ten microns of mercury (1/76,000 of an atmosphere), then hydrogen gas is introduced into the furnace to remove residual oxygen. After the molten nickel has been held

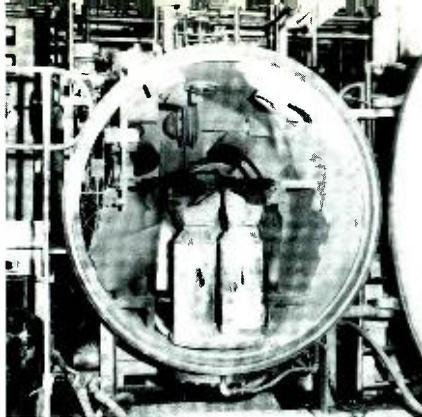


Fig. 3—RCA-operated 500-pound vacuum melting furnace, showing interior of vacuum chamber and two ingot molds positioned to receive melted nickel alloy.

for ten minutes in an atmosphere of hydrogen at a pressure of 20 millimeters of mercury, the hydrogen and the water vapor, which has formed as a result of the oxide reaction with the hydrogen, are pumped off and the vacuum of ten microns is restored. Pure argon (an inert gas) is subsequently introduced into the furnace to a pressure of 1/3 of an atmosphere and the alloying agents are successively added to the melt. The removal of oxygen from the molten nickel by hydrogen treatment and the subsequent prevention of oxygen contamination by the use of an argon atmosphere are the most important steps in the vacuum melting process.

During the process, the temperature of the melt is controlled to values that are within $\pm 5^\circ$ C and the time of addition of each ingredient and the time of pouring are both controlled within seconds. Although most of the additives have low vapor pressures at the temperature of the melt, some, particularly magnesium, are volatile and thus escape from the melt at a certain rate. However, the loss is held constant by means of accurate control of time, temperature, and gas pressure. For compensation for the loss, the amount of additives added to the melt is chosen so that the required amount is retained in the alloy. Most addition elements used in the alloys are not troublesome in this respect. Carbon, cobalt, manganese, silicon, and tungsten do not present this problem; what is added to the melt is found in the ingot.

One of the great drawbacks associated with standard commercial melting practice is the segregation of different components within the finished ingot. Segregation occurs in very large ingots poured from very large melts, because solidification is so slow that high-purity nickel crystallizes out

from the melt first and the additives are driven ahead of the solidification front in such a manner as to create inhomogeneity in the resulting ingot. For this reason, a limit of the ingot size is important in the production of homogeneous material. Experience has shown that a 250-pound ingot, of which two are poured from each 500-pound melt, is small enough to solidify rapidly and not allow segregation to take place.

ROLLING THE INGOT TO STRIP

One of the major difficulties encountered in producing reproducible cathode strip is the control of the reduction of the ingot to strip. This work is done outside RCA, not under our direct control. It has been found that much more care is needed to produce good cathode strip than is required in the normal rolling-mill practices applied to the processing of most commercial alloys.

Because all rolling is done in air and part of the initial reduction in thickness is carried out at high temperature (hot-rolling), carbon, which has a very high diffusion speed in nickel, is lost due to oxidation by the oxygen in the air. This loss is compensated for by the addition of more carbon to the melt than is needed in the finished strip. The loss of carbon during the annealing stages that comprise part of the final cold-rolling process must also be controlled so that the carbon specification on the strip used to make cathodes is rigidly maintained. Although carbon is not closely controlled in most commercial nickel alloys, cathode nickel requires control within a few hundredths of a percent. Too much carbon causes gassy tubes. Too little carbon indicates that the strip has been exposed to excessive oxidation, and that probably some of the other reducing agents, which are vital to the electron emission behavior of the tube, have been oxidized.

NEW ALLOY DEVELOPMENT

The development of cathode alloys having improved characteristics is a job that is never finished. As the tube requirements become more strict for such factors as behavior during vibration, longer life, higher dissipations, and higher ambient temperatures, cathode materials must be improved

accordingly. Vacuum melting and reproducible composition are the prerequisites. Work in the Chemical and Physical Laboratory is pointing the way to cathode materials having greater stability of emission throughout life, absence of interface impedance and of evaporation products, and higher strength at operating temperatures.



DR. IRVING F. STACY received the A.B. degree in Chemistry from Brooklyn College in 1941, and the A.M. and Ph.D. degrees in Physical Chemistry from Columbia University in 1949 and 1954, respectively. From 1942 to 1944 and from 1946 to 1947 he worked on instrumental methods of analysis in the Test Laboratory at the Philadelphia Naval Base. He served as electronic technician in the U. S. Navy from 1944 to 1946. At Columbia University he was research assistant and graduate assistant in instrumental analysis. Since 1954, Dr. Stacy has been in the Receiving Tube Chemical and Physical Laboratory at Harrison, working in the fields of thermionic emission and mass spectrometry. He is a member of Sigma Xi, the American Chemical Society, the American Vacuum Society, and the Institute of Radio Engineers, and is an RCA representative in the American Society for Testing Materials.

C. W. HORSTING received the B.S. degree in Chemistry in 1934 and the M.S. degree in Physical Chemistry in 1938, both from the University of Utrecht in the Netherlands. He came to the United States in 1940, and joined RCA two years later as a member of the Metallurgy group in the Chemical and Physical Laboratory of the Electron Tube Division in Harrison. From 1942 to 1951, he worked on such problems as carburization of thoriated-tungsten filaments, electron-tube cathode alloys having high strength at elevated temperature, metal-tube mainseal welding, and electron-emission problems. He was instrumental in the introduction of vacuum melting for the production of cathode alloys. In 1951 he became Engineering Leader in charge of the Metallurgy group at Harrison. In 1958 he became responsible for Metallurgy, Engineering Development. Mr. Horsting is a member of the American Society for Metals and the American Institute for Mining and Metallurgical Engineers.



RADIOTRACERS IN PARTS-CLEANING EVALUATION*

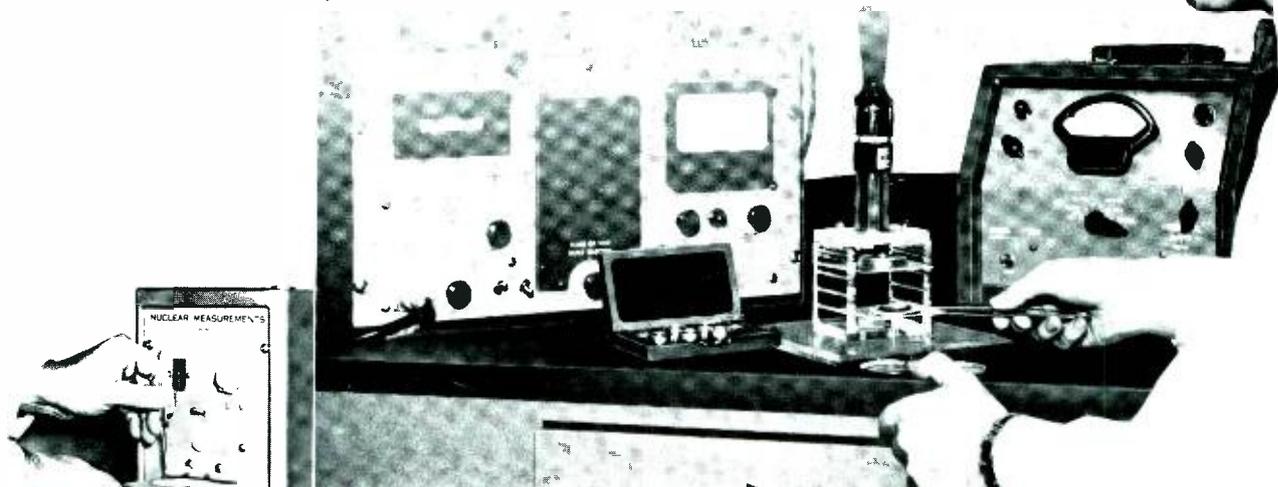
by

M. N. SLATER

*Silicon Rectifier Design Engineering
Semiconductor and Materials Division
Lancaster, Pa.*

DR. D. J. DONAHUE, Mgr.

*Advanced Semiconductor Chemistry and Physics
Semiconductor and Materials Division
Somerville, N. J.*



MORRIS N. SLATER received the B.Sc. degree in General Science from the University of Manitoba, Canada, in 1945, and has done graduate work in physical and organic chemistry, mathematics, and radiochemistry at the University of Minnesota and Purdue University. While attending graduate school, he worked part time as a research assistant on N.O.R.D. rocket-fuel research, on radium, radon, and radiotracers, and on textile research and development. From 1950 to 1951, he worked at the Gates Rubber Company in Denver, Colo. on analytical development and research on coatings and adhesives. He joined the RCA Electron Tube Division in Marion, Indiana in 1951 as a design and development engineer in the Chemical and Physical Laboratory, and transferred to the Lancaster Chemical and Physical Laboratory in 1956. His work included kinescope glass-to-metal sealing, filming, aluminizing, coatings, adhesives, parts cleaning, and radiotracers. Since 1958, he has been a member of the Silicon Rectifier Design activity of the Semiconductor and Materials Division in Lancaster. Mr. Slater is Chairman of the Lancaster Great Books Committee.

LORD KELVIN is reported to have said, "When you can measure what you are talking about and can express it in numbers, you know something about it." It was for this reason—to attach numbers to qualitative concepts of degree of cleanliness—that studies on the use of radiotracers in parts-cleaning evaluation were started and are still going on.

This paper reports the results of two studies in this series: the first was the conventional situation of the removal and redeposition of an inorganic salt by water; the second was the specific problem of the removal of etchant-acid residues from electron tube cathode sleeves.

DR. D. J. DONAHUE studied Physical Chemistry at the University of Michigan, receiving the B. S. degree in 1947, the M. S. degree in 1948, and the Ph.D. degree in 1951. He joined the RCA Electron Tube Division in Lancaster in 1951, and spent the next seven years working on chemical and physical problems involved in the design of the color television picture tube, including fine-mesh screens, transparent conductive coatings, aperture masks, and the application of phosphor screens. He also set up the surface and radiotracer laboratory, and worked on problems involving cathodes, conductive coatings, and parts cleaning. He transferred to the Semiconductor and Materials Division in Somerville in 1958, where he is presently Manager of Advanced Semiconductor Chemistry and Physics. His responsibilities in this position have included the study of semiconductor surfaces, diffusion masking, purification of gallium and arsenide, solid-state measurements, and new devices.

While these results are interesting and useful in themselves, their greatest importance lies in the fact that a base line has been established which can lead to a thorough quantitative understanding of contamination and cleaning.

BACKGROUND

The classical method studying parts cleaning has consisted of weighing parts before and after various cleaning procedures and comparing the weights to determine the amount of soil removed. The normally low ratio of soil weight to part weight and the consequent lack of sensitivity of this technique often neces-

sitated prior addition of exaggerated, relatively massive amounts of soils, which made the validity of the results questionable.

The atomizer spray-wetting technique recently developed and described² reportedly permitted estimation of residual organics to a fraction of a monolayer, but appeared to be limited so far to organic residues and to non-absorbent surfaces of regular conformation. Furthermore, it allowed for little or no manipulation of the part.

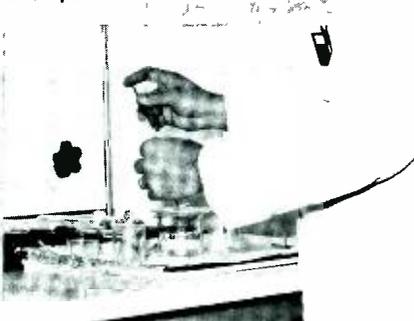
The radiotracer technique offers a unique method for following specific kinds of contaminants in near-molecular quantities through specific processing steps with precise measurement of the amounts remaining. The extreme sensitivity of detection permits the use of contamination levels identical with those found in actual production. This sensitivity and the rapid non-destructive measurements permit examination of parts and processes without effect on either, thereby enhancing the authenticity and applicability of the results. Some of the typical techniques and equipment involved are illustrated in Fig. 1.

Some previous work in metal cleaning by Harris^{3,4}, Hensley^{5,6,7}, and others, using radioactive soils to evaluate detergent systems, while not directly applicable, provided some valuable insights and techniques.

*Describes work done while authors were with the Electron Tube Division, Lancaster, Pa. As noted at the end of article, these studies are being continued by the Electron Tube Division.



Fig. 1—Far Left: M. N. Slater places a sample in a windowless gas flow counter. Left Center: Dr. D. J. Donahue with counting equipment (multiscaler, Geiger-Muller counter and sample holder, and count-rate meter). Top: Radiotracer-tagged material is removed from lead-brick storage vault prior to manipulation. Bottom: A syringe and a pipette are used to contaminate a test part.



REMOVAL OF INORGANIC CONTAMINANTS

In the first study, the contaminant used was sodium sulfate, labelled with S^{35} . This material was selected because it is easily and safely manipulated, readily obtained, and inexpensive. For simplicity in this initial study, the "parts" were 18-12 stainless-steel disks, 1.875 inches in diameter and 0.015 inch thick, electropolished, and essentially scratch-free at 500X magnification. The sample parts were contaminated with the tagged sodium sulfate, washed under controlled conditions, dried, counted, then rewashed, redried, and recounted until the tests were completed.

Contamination

The S^{35} was received from the supplier in a glass vial as sulfate in dilute hydrochloric acid. Next, ordinary sulfuric acid was added, and the combination was thoroughly mixed and allowed to stand for several days to permit exchange with any material adsorbed on the walls. The mixture was then transferred to a larger flask, and a stoichiometric amount of aqueous sodium hydroxide solution was added to make the stock solution of sodium sulfate.

Just before use, the parts were soaked in concentrated sulfuric acid, rinsed with deionized water, and dried under an infrared lamp. The parts were contaminated by micropipetting the stock solution on each part, spreading it over the

surface with a loop of 0.030-inch nichrome wire, and drying it in air. A reasonably uniform and nearly invisible layer of approximately 0.4 milligram or 200 monomolecular layers of sodium sulfate was deposited on each part.

Washing

The washing was performed by dipping the part for 3 minutes into 100-milliliter portions of fresh deionized water in 150-milliliter beakers maintained at the test temperature. At the end of each dip period, the part was removed, allowed to drain for 5 seconds, then laid flat on a 3-point support and air-dried.

Counting

Initially and after each dip the residual radioactivity of the part was counted in a windowless gas-flow proportional counter (actually used in the Geiger-Muller region) having a counting geometry of 2π . Total counting efficiency was approximately 80 percent including backscatter. P-10 counter gas (90 percent argon, 10 percent methane) was used. The counter was connected through a preamplifier to a multi-scaler. The claimed counter resolution time for this system was 0.1 microsecond, and the scaler resolution time was 0.5 microsecond.

Almost all counts were made by the tedious but most accurate method of interleaved measurements, i.e., a background measurement was made before and after each sample and the average was used to correct the sample. Only when the background was negligible, i.e., less than one percent of the sample count, was the alternate method used: a background measurement after every five samples. More than 10,000 counts were taken for most samples and, when necessary, cumulative background counts of 10,000 or more. No sample count was less than 2,000.

Results

The results are shown in Fig. 2 (left and right). Each point represents the aver-

age of 2 to 5 determinations. Fig. 2 (left) is the results of the first test run, which consisted of three successive dips of 3 minutes each at temperatures of 22, 58, and 97°C. and in boiling water. There was no agitation of the parts during washing. The point marked "Factory Process" shows the result obtained when a tagged part was mixed with a batch of standard parts and put through an analogous factory cleaning process of three dips of 3 minutes each at 90°C.

Because it was felt that the lowest points on these curves were below the limits of counting accuracy, the test was repeated with a new stock solution having ten times the specific activity, i.e., ten times as much radioactive material and, therefore, ten times as many counts for the same amount of total sulfate. Fig. 2 (right) is the results of this second run, which consisted of five dips of 3 minutes each at 26 and 58°C. and in boiling water. In this run, the parts were continuously agitated by hand during washing.

Recontamination

Recontamination of parts by impure solvents was also of considerable interest. Clean parts were dipped into solutions of known concentration of the labelled sulfate. This test was also run with methanol solutions. The results are shown in Fig. 3. Both curves were determined at room temperature (22°C.).

Conclusions

The following conclusions can be drawn from the test results:

Higher water temperature aided in removal of the sulfate.

Agitation produced some improvement in sulfate removal at the lower temperatures, none in the boiling water. This result was expected because of the agitation provided by the boiling itself.

More dips at a given temperature removed more sulfate, but with a rapidly diminishing effect. This result indicated a kind of partition coefficient at each

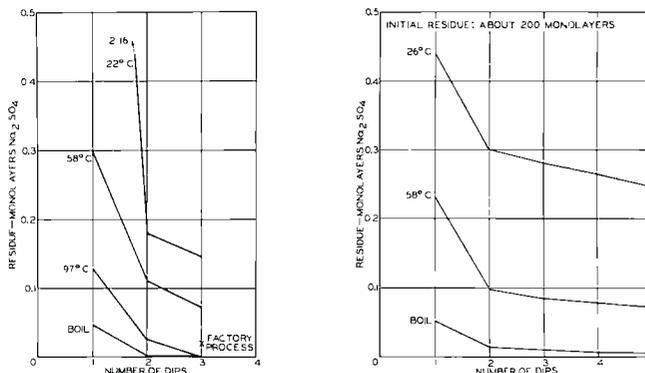


Fig. 2—Left: Removal of sodium sulfate from parts by water; 3-minute dips; no agitation; first run. Right: same, except continuous agitation; second run.

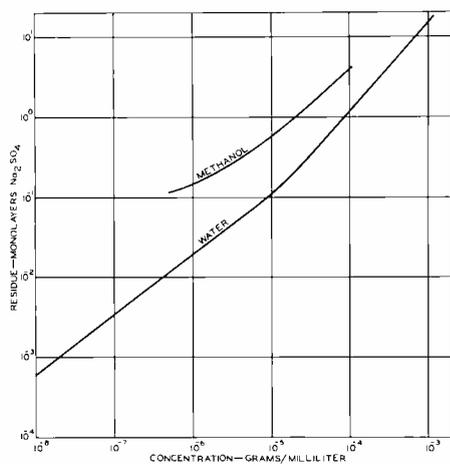


Fig. 3—Recontamination of parts by cleaning media; 3-minute dips; no agitation; room temperature (22°C).

temperature between the solubility of the sulfate in water and its adsorption on the surface of the steel.

Clean parts were recontaminated by impure cleaning solutions. The degree of recontamination was proportional to the concentration of the contaminant in the solution. The greater deposition from equivalent concentrations in methanol was expected because of the lower solubility of the sulfate in methanol and the consequent difference in the partition coefficient for this system. This effect emphasizes the importance, in evaluation of a cleaning system or solvent, of considering the solubilities of impurities as well as their concentration, and also their possible affinity for the part to be cleaned.

REMOVAL OF ACID RESIDUES FROM CATHODE SLEEVES

The life of the cathode is one of the most important parameters determining the life of an electron tube. Extremely small amounts of impurities can severely limit the emission and shorten the life of oxide-coated cathodes. Consequently, the cleaning of parts designed for use inside the tube is very important and has received a great deal of attention. Maximum attention has naturally been given to the cleaning of the cathode sleeve itself.

One of the processes for cleaning cathode sleeves included an acid treatment with a mixture of acetic and nitric acids. This study was initiated to determine the efficacy of subsequent washing steps in removing the acid and to compare these procedures with proposed new methods such as ultrasonic cleaning. Standard electron-tube nickel cathodes were used for these tests.

Sample cathodes were treated with radioactive acid and mixed with regular lots of cathodes treated with ordinary standard acid. The cathodes were then

processed by the various cleaning techniques, the two types were separated, and the remaining radioactivity of the sample cathodes was measured as an index of the residue. Acetic acid, labelled with C^{14} at the carboxyl carbon, was selected as the tracer material.

The cleaning process used as the basis for this study consisted of the following steps:

1. Two boiling-water rinses.
2. Two methanol rinses.
3. One 10-minute boiling-acid treatment.
4. Ten to fifteen water rinses.
5. Two methanol rinses.
6. Air-drying.
7. Hydrogen-firing.
8. Sizing.
9. Ether rinse.
10. Two boiling-water rinses.
11. Two methanol rinses.
12. Air-firing.
13. Hydrogen firing.

The acid treatment (step 3) is the point at which the radiotracer material was introduced. Steps 4 (rinse), 7 (hydrogen-firing), and 12 (air-firing) were selected as the most important in removal of the acid. The standard acid contained: 20-percent glacial acetic acid (by volume), 1-percent dilute nitric acid (20-percent concentrated nitric acid in water), and 79-percent water.

Key techniques in these steps, to be described in the following paragraphs, are illustrated in Figs. 4 through 13.

Washing

The radioactive acetic acid was received from the supplier in a pyrex tube sealed with a break-off septum (Fig. 4). This tube was sealed to a closed-end Liebig condenser (Fig. 5), the septum was broken, and the acid was transferred by immersing the bottom of the condenser in liquid air and heating the tube. The tube was then sealed off. Inactive stand-

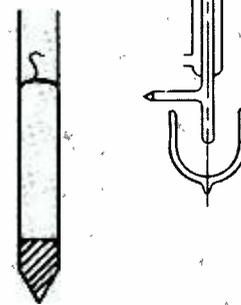


Fig. 4—Radioactive acetic acid sealed in tube with break-off septum.

Fig. 5—Sealing of acid tube to a closed-end Liebig condenser.

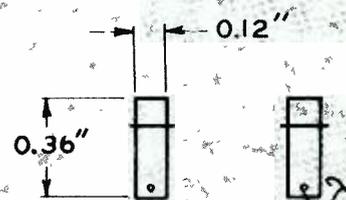


Fig. 6—Identification of tagged cathodes by nickel wire.

ard acid was added to the condenser by pipette to obtain proper acid composition and volume.

A small loop of nickel wire was attached to each of the tagged cathodes so that the few tagged ones could be identified among thousands of others (Fig. 6). The parts were washed in water and methanol according to steps 1 and 2 above. The acid was heated to 100°C. by immersing the end of the condenser in boiling water. The cathodes were treated by lowering them on a long loop of nickel wire into the heated acid (Figs. 7 and 8). They were left in the acid for 10 minutes, then withdrawn, shaken free of excess acid, and mixed with a lot of 25,000 cathodes which had simultaneously been put through the water, methanol and acid washes. The entire lot was then divided into separate test runs and immediately run through subsequent test steps (Table I).

After completion of each test, the parts were rinsed in methanol and air-dried. The tagged cathodes were separated, taken to the laboratory in closed

TABLE I. WASHING METHODS

| Run No. | Washing Method |
|---------|---|
| 1 (a) | Standard—ten cold-water rinses |
| 1 (b) | Ultrasonic, hot—four cold-water rinses plus one 10-minute ultrasonic rinse with circulating hot (140 to 150 degrees fahrenheit) water |
| 2 (a) | Standard—ten cold-water rinses |
| 2 (b) | Ultrasonic, cold—four cold-water rinses plus one 10-minute ultrasonic rinse with circulating cold water |
| 2 (c) | Ultrasonic, hot—four cold-water rinses plus one 10-minute ultrasonic rinse with circulating hot (140 to 150 degrees fahrenheit) water |
| 2 (d) | Hot—four cold-water rinses plus one 10-minute rinse with circulating hot water |

Fig. 8—Immersing cathodes into heated acid.

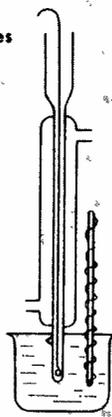


Fig. 7—Attachment of cathodes to nickel-wire loop.



Fig. 9—Slitting open and flattening of cathodes to allow counting of inside and outside of cathode-sleeve surfaces.

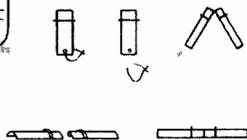


Fig. 10—Nickel pan for hydrogen-firing.

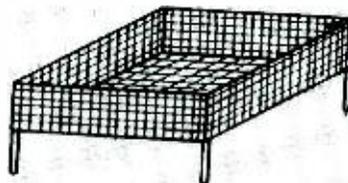
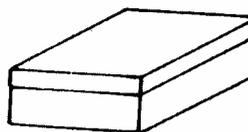


Fig. 12—Stainless-steel wire-mesh basket for air-firing.

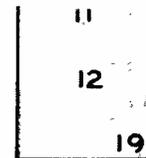


Fig. 11—Arrangement of tagged cathodes in pan.

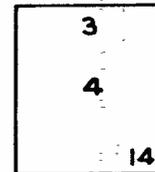


Fig. 13—Cathode arrangement in basket for air-firing.

glass vials, and measured for residual radioactivity.

The effect of the various cleaning steps on the inside of the cathode cup as compared to the outside was determined as follows: several of the cathodes were slit open and flattened, and the wire loops were removed, as shown in Fig. 9. The "inside" and "outside" cathode-sleeve surfaces were then counted.

Firing

Hydrogen-Firing: Tagged cathodes were placed in the bottom layer of a solid nickel pan (Fig. 10) normally used for this purpose and arranged as shown in Fig. 11. The purpose of this arrangement was to permit identification of individual parts after firing. The tagged cathodes were covered with approximately 6,000 other cathodes, and all were fired in a Hayes furnace for 10 minutes at 1,000°C. in line hydrogen (−20°C. dew point).

Air-Firing: Tagged cathodes were placed in the middle layer of approximately 2,000 cathodes in a stainless-steel wire-mesh basket (Fig. 12) and arranged as in Fig. 13. The parts were then put into a Hoskins furnace which had been preheated to 800°C; the parts

were left in 10 minutes, removed, and cooled. The counting procedure and equipment was the same as that described above.

Results

The results obtained are summarized briefly in Table II. Each point represents the average of a minimum of three tagged parts.

Discussion

Hot-water rinsing was very significantly better than cold-water rinsing for removal of acetic or acetate residues after acetic-acid treatment of cathodes.

Ultrasonic rinsing with cold water was approximately equivalent to hot-water rinsing for external cleaning, but significantly better for internal cleaning.

Ultrasonic rinsing with hot water was very significantly better than ultrasonic rinsing with cold water. *This was the best method tested.* It was far superior in reducing the total residue and, most important, in reducing the internal residue.

Ultrasonic rinsing, hot or cold, was significantly better than comparable rinsing without ultrasonics, particularly in removal of residues from the hard-to-reach interior of the deep-drawn cathode cup.

Hydrogen-firing very significantly reduced the amount of contaminant left on the parts.

Air-firing very significantly reduced the amount of contaminant left on the parts. It was probably the most effective single step in the removal of organic residues. This result is in apparent agreement with some of the results given by Feder and Koontz.²

SUMMARY

Both of these studies demonstrated the unique advantages of the radiotracer method: Extreme sensitivity of measure-

ments (down to 0.005 monomolecular layers in the sulfate study, with another 2 or 3 orders of magnitude readily available) combined with extreme simplicity of technique.

Although the work with acetic acid is essentially completed, the work with the sulfate is only a beginning. Planned areas of investigation include: organic contaminants and other cleaning systems; mixed contaminants, organic and inorganic; effect of surface condition, probably the most fruitful and most important area in the series of studies; migration of contaminants in devices; and correlation of the contaminant (kind, amount, location) with device quality and life.

The authors gratefully acknowledge the assistance and advice of S. Kitagawa, E. L. Romero, and Dr. C. H. Thomas.

REFERENCES

1. E. B. Ashcraft, "Use of Radioactive Tracers in the Study of Soil Removal and Detergency," Symposium on Radioisotopes, p. 30, ASTM (1958) STP No. 215.
2. D. O. Feder and D. E. Koontz, "Detection, Removal, and Control of Organic Contaminants in the Fabrication of Electronic Devices," Symposium on Cleaning of Electron Device Components and Materials, ASTM (1958) STP No. 246.
3. J. C. Harris, R. E. Kamp, W. H. Yanko, "Application of the Radioactive Tracer Technique to Metal Cleaning," ASTM Bulletin No. 158, May 1949, p. 49 (TP75).
4. J. C. Harris, R. E. Kamp, W. H. Yanko, "Improved Radioactive Tracer Carrier for Metal Cleaning Studies," ASTM Bulletin No. 170, Dec. 1950, p. 82 (TP308).
5. J. W. Hensley, H. A. Skinner, H. R. Suter, "A Metal Cleaning Test Using Radioactive Stearic Acid as Soil," Papers on Evaluation of Soaps and Detergents, p. 18, ASTM (1951) STP No. 115.
6. J. W. Hensley, "Radioactive Tracers Track Metal Cleaner Effectiveness," Iron Age, 170, 151 (1952).
7. J. W. Hensley, "Radioactive Tracers Track Metal Cleaner Effectiveness," Plating, 40, 366 (1953).

TABLE II.
AVERAGE RESIDUES AFTER CLEANING

| Process | As Monolayers of Acetic Acid | Ratio, Inside/Outside |
|------------------|------------------------------|---|
| Standard | 25.6 | 6.66 |
| Ultrasonic, cold | 0.68 | 2.47 |
| Ultrasonic, hot | 0.09 | 2.13 |
| Hot | 0.86 | 6.54 |
| | | Residual contamination after firing (percent) |
| Hydrogen firing | 0.40 | 2.0 |
| Air firing | 0.009 | 0.03 |

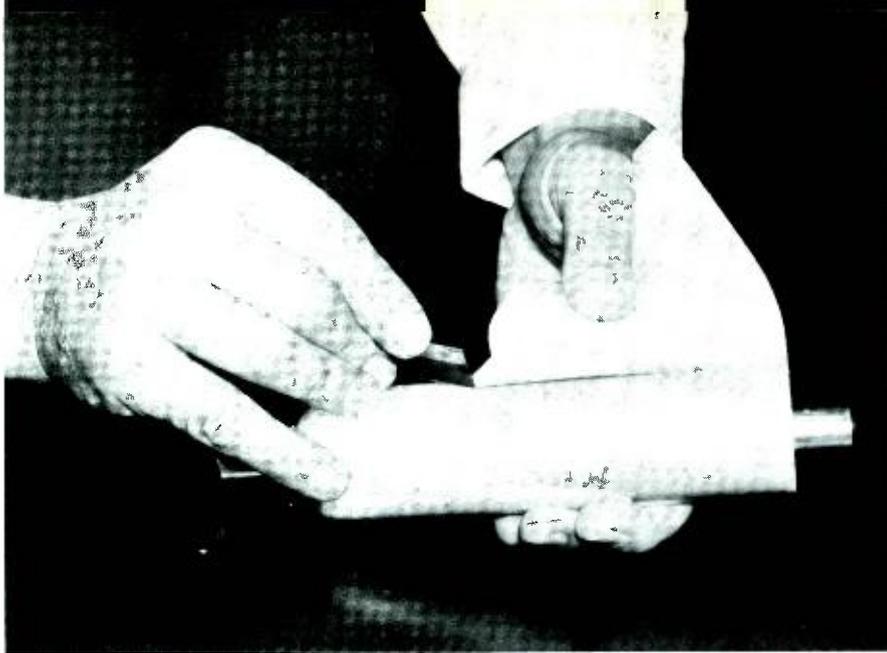


Fig. 1—A conductive rubber roller is cut out of a polyethylene mold. The rubber material is a special conductive type formulated and fabricated in the DEP Chemistry Laboratory.

CONDUCTORS FROM NONCONDUCTORS— ADHESIVES, COATINGS, PLASTICS, PAPERS, AND RUBBERS

by

DR. L. H. CUTLER

Materials Standards Section
Central Engineering
DEP, Camden, N. J.

IN THIS MODERN electronic age, the need has arisen for making normally nonconductive materials electrically conductive—papers, paints, rubbers, plastics, and adhesives. The art of converting normally nonconductive materials into conductors has been known for many years, but has been of little importance until recently. In the familiar Leclanché dry-cell batteries, for example, cathodes are made of manganese dioxide—a poor conductor; conductivity is improved by the addition of a small amount of carbon black to the mix during manufacture, resulting in batteries of lower internal resistance.

SOME BASIC TECHNIQUES

More recently, RCA^{1,2} has developed a number of highly successful dry-cell batteries employing nonconductive cathode materials having high electrical-energy capacities. In their original form, these materials would be unsuitable, since batteries containing them would have an infinite internal resistance. So, by mixing 33 to 50 percent, by weight, of carbon black with these

materials, satisfactory batteries with low internal resistances have been manufactured.

A number of these nonconductive materials have such high capacities that even after the addition of carbon, they still give more electrical energy than the conventional cathode materials on a weight and volume basis. Derivatives of nitrobenzene and the new halogen laundry bleaches such as dichlorodimethylhydantoin, trichloromelamine, and hexachloromelamine are examples of normally nonconductive materials made conductive by this technique and thus suitable for use in batteries.

This same technique has been applied in making other materials conductive. Conductive papers required in the Electrofax process were provided by adding carbon black to the pulp during the manufacturing of the paper. Conductive papers could also be used as gasketing material and may be of use in other applications. One manufacturer (Knowlton Brothers, Watertown, N. Y.) will cooperate in the development of special conductive papers.

Vinyl Plastics

Another commercially available material is a conductive vinyl plastic. Here again, the normally nonconduc-

tive vinyl plastic is made conductive by the addition of carbon black during manufacture. The material is available in pellet form to be processed by the user, in calendered sheet, film, and tape form in various widths and thicknesses, or in liquid form for roller or knife coating, brushing, spraying, and laminating.

It is interesting to note that RCA pioneered the use of conductive vinyl over 20 years ago. Carbon was introduced in the manufacture of vinyl transcription records to give them conductivity in order to prevent static charge build-up, which attracts dust and results in noise.

Today, conductive vinyl has found use as an electrostatic shield, replacing copper braid in communication cables, as shielding on microphone cables, as a conductor in an interference-suppression automobile ignition cable, and as shielded wire for coaxial and high-voltage cables. The material can also be used in antistatic devices, conductive gasketing, de-icing in aircraft, and many other applications.

The Abbey Plastic Corporation, Hudson, Mass., which supplies the pellets as *Abbey #100 Conductive Vinyl*, lists the physical properties³ shown in Table I.

TABLE I—PHYSICAL PROPERTIES,
ABBAY #100 CONDUCTIVE VINYL

| | |
|---|-------|
| Resistivity, ohm-cm. | 11 |
| Tensile Strength, psi | 1500 |
| Modulus at 100% elongation, psi | 1450 |
| Cold bend (50 mil slab, 180° bend, ½" mandrel) | -40°C |
| Elongation, % | 125 |
| Durometer (Shore A) | 88 |
| Specific Gravity | 1.39 |

A number of conductive rubber materials having similar properties and uses are also commercially available. Here again, conductivity is achieved by the addition of carbon black.

Adhesives

The use of carbon in making materials conductive has recently been extended to the adhesive field. Emerson & Cuming, Inc., Canton, Mass., introduced two adhesives containing carbon: *Eccobond 60C* and *Eccobond 60L*. The *Eccobond 60C* is a one-part 50-ohm-cm material cured at 300 to 500°F; the *Eccobond 60L* is a two-part 50-ohm-cm material cured at room temperature to 300°F. Both

materials are used for general-purpose bonding where electrical conductivity must be maintained. The materials have been used to make good metal-to-metal joints so to eliminate r-f cabinet leakage. These materials can also be used to assure an intimate electrical bond between adjacent waveguide flanges. *Eccobond 60C* or *Eccobond 60L* can be externally applied in thin coatings to absorb or attenuate currents flowing on the surface of electrical conductors. These materials exhibit excellent thermal conductivity, comparable to that of steel, and therefore, they are useful in applications where high heats are dissipated. The manufacturer lists^{4,5} the properties for these materials shown in Table II.

HIGH-CONDUCTIVITY APPLICATIONS

Though carbon is very useful, inexpensive, and readily available, the conductivity that can be introduced in a material by blending it with carbon is limited by the conductivity of the carbon itself. For applications requiring high conductivity, silver powder is used in place of carbon black. Of course, the cost of silver powder is substantially greater than carbon. The use of metal pigments in paints is well known, for example, in aluminum paint and the decorative bronzes. These metal pigments, however, are coated with an oxide film, making them poor conductors.

Coatings

The silver paints manufactured by DuPont Electrochemical Dept., Wilmington, Delaware, and Handy & Hartman, New York, N. Y. are similar to aluminum and bronze paints, but

TABLE II — PROPERTIES OF ECCOBOND 60C AND 60L CARBON CONDUCTIVE ADHESIVES

| Property | 60C | 60L |
|--|----------------|----------------|
| Temperature Range for use | -70°F to 500°F | -70°F to 350°F |
| Bond Shear Strength, 1" overlap of Aluminum Plate, psi (Bond Strength was unaffected by 30 days water immersion) | | |
| Room Temperature | 3400 | 3000 |
| -70°F | 2700 | 2300 |
| +200°F | 1700 | 1100 |
| Flexural Strength, psi | 12000 | 6000 |
| Volume Resistivity, ohm-cm: | | |
| Room Temperature | approx. 50 | approx. 50 |
| 200°F | approx. 50 | approx. 50 |
| Thermal Conductivity, BTU/sq. ft./in./°F | 195 | 190 |
| Dielectric Constants at frequencies of: | | |
| 10 ⁶ cps | 6000 | 5000 |
| 3 × 10 ⁹ cps | 20 | 35 |
| 10 ¹⁰ cps | 25 | 39 |
| Dissipation Factors at frequencies of: | | |
| 10 ⁶ cps | 20.0 | 15.0 |
| 3 × 10 ⁹ cps | 1.5 | 1.6 |
| 10 ¹⁰ cps | 2.0 | 0.63 |

contain powdered silver flake. The silver does not tend to oxidize and is an excellent conductor, even in powdered form; hence, the coatings obtained using these silver paints results in excellent conductors. These paints are designed to place a thin conductive coating on normally nonconductive materials which, in turn, could be used as a base for plating, soldering, or painted wiring.

Basically, these conductive coatings consist of 30- to 70-percent silver powder and a bonding agent. There are two types commercially available:

One consists of silver powder mixed with a powdered-glass-frit bonding

agent and dispersed in an organic vehicle. This type of coating requires a firing temperature of 750 to 1700°F to burn off the organic vehicle and fuse the glass, giving a continuous film. It is limited to materials capable of withstanding this extremely high temperature, but yields an extremely adherent film having a high conductivity—up to 75 percent of the conductivity of solid silver with the equivalent weight and shape.

The second type consists of silver powder mixed with a thermoplastic or

DR. LEONARD H. CUTLER received the B.S. in Chemistry in 1949 from the Philadelphia College of Pharmacy and Science, and the M.S. degree in Physical Chemistry in 1950 and the Ph.D. degree in Physical Chemistry in 1952 from the University of Delaware. He held a Research Fellowship at the University of Delaware from June 1949 to July 1952. Dr. Cutler served in the U. S. Navy from March 1943 to January 1946, and was honorably discharged with the rank of Electronics Technician's Mate First Class. From July 1952 to December 1953 he was employed by the U. S. Steel Corporation in Pittsburgh, Pa., as an electrochemist working on problems involving the corrosion of metals. In December 1953 he joined the Chemical Laboratory of RCA in Camden, N. J. and has worked on a variety of physical chemistry projects. He is a member of the American Chemical Society. He has presented several papers at technical meetings and has had a number of technical articles published.



Fig. 2—The author, Dr. L. H. Cutler (foreground), and a laboratory technician, R. J. Forster, measuring changes in conductivity of a conductive adhesive as tensile stress is varied.

TABLE III — PROPERTIES OF SILVER CONDUCTIVE ADHESIVES

| | <i>Eccobond</i> 58C | <i>Eccobond</i> 56C | <i>Hysol</i> 6250 |
|-----------------------------|------------------------|------------------------|----------------------|
| Type | 1 component | 2 component | 2 component |
| Cure temperature | 300-500°F | 120-250°F | R.T.-140°F |
| Use temperature after cure | -65-1000°F | -70.+350°F | — |
| Volume resistivity, ohm-cm. | Below 0.1 | Below 0.1 | 0.01 |
| Bond sheer strength, psi | 3200 | 2900 | 2000 |
| Flexural strength, psi | 9700 | 12200 | — |

thermosetting organic-resin binder. These materials can be air-dried or dried at slightly elevated temperatures. The thermosetting type requires baking at 300 to 400°F. These coatings are fairly conductive, having 5 to 25 percent of the conductivity of solid silver of the equivalent weight and shape. Adhesion of the film, though relatively poor, is adequate for bonding to the base material.

Adhesives

Silver-powder adhesives are similar to the air-dried conductive coatings in that they consist of fine silver powder dispersed in an organic resin bonding agent. These adhesives are used to bond together materials where high conductivity is needed in the bond, rather than to apply a conductive surface film as those obtained by using the conductive air-dried silver paints. In conductive adhesives, the organic resin binders are epoxy based and adhere excellently to metals, glass, plastics, and ceramics.

The conductive adhesives are air-dried or cured at slightly elevated temperatures. They are used as replacements for solder in applications requiring electrical conductivity yet where soldering temperatures cannot be tolerated; for example, in bonding to nichrome wire, to conductive plastics, or to thin-metal plates. The conductive silver adhesives have high thermal conductivity and are, therefore, useful in applications where high heats are dissipated. Among the commercially available low-resistance silver conductive adhesives are *Eccobond 58C* and *Eccobond 56C* manufactured by Emerson and Cuming, Inc., and *Hysol 6250* manufactured by Houghton Laboratories, Inc., Olean, New York.

These manufacturers^{6,7,8} list the properties shown in Table III.

SPECIAL FILMS AND INKS

First, there are the carbon inks and paints, materials which are similar to the silver coatings. These are used to apply a thin film of material containing carbon onto a nonconductive substrate such as glass or ceramics. Thin films of carbon have a fairly high resistance (over 50 ohms per square) and are thus generally used as film resistors in electronic applications. Carbon films deposited directly from a flame by pyrolysis present high resistance and are similarly used as resistors in electronic applications.

Inks of precious metals and precious metal organometallics are also commercially available. Among the metals used in these inks are gold, platinum, and palladium. Inks are sprayed or painted on glass or ceramics and then fired at high temperatures—over 1000°F. Depending on the type and concentration of the metal in the ink, resulting films vary in conductivity from good conductors to values low enough to be used as resistors. Since these inks are very expensive and contain precious metals, they are used only where a high cost can be justified, as in chemically-inert electrical contacts. Hanovia Chemical and Mfg. Co., East Newark, New Jersey, specializes in the manufacture of these inks.

Films of many materials can also be applied in varying thicknesses to nonconducting substrates by metal evaporation techniques. Here again, the conductivity can be varied from very high values to very low conductivity values, making the films useful as resistors in electronic applications.

Another type of conductive film that can be deposited on glass and ceramics is the tin oxide film. Such films vary in resistance from 20 to 200 ohms per square depending on film thickness. Because these films are still

transparent when applied to glass, they have been used in aircraft windshields to carry current for de-icing. They are widely used as heating elements in small space heaters in the home and have found use as commercially available resistors in electronic applications. The film is deposited by heating the substrate to over 1100°F and then spraying it with a mist of tin chloride solution which is instantly reduced to the conductive tin oxide coating. Tin-oxide-coated plate glass is commercially available.

CUSTOM APPLICATIONS

For special applications requiring tailor-made products, conductive powders are available to the user for his own formulations. Practically any paint, plastic, adhesive, rubber or other insulating material can be made conductive. For example, Godfrey L. Cabot, Inc., Boston, Mass., Shawinigan Chemicals Limited, Shawinigan Falls, Quebec, Canada, and Witco Chemical Company, New York, New York, and many other companies manufacture a high-conductivity carbon black. Handy and Harman, New York, New York and Metals Disintegrating Company, Elizabeth, New Jersey are among the manufacturers of fine powdered silver flake designed for use in making materials conductive. Many manufacturers produce precious-metal powders.

Finally, laboratories close to the product development engineer—the Materials Standards Section of DEP Central Engineering is a specific example within RCA—can and have developed many special conductive materials for specific applications.

BIBLIOGRAPHY

1. Morehouse, C. K., and Glicksman, R. "Dry Cells Containing Various Aromatic Nitro Compounds as Cathode Materials," *Journal of the Electro-chemical Society*, vol. 105 (June, 1958), pp. 306-311.
2. Lozier, G. S., Cutler, L. H., and Morehouse, C. K. "Organic N-Halogen-Magnesium Reserve Batteries," *Extended Battery Abstracts of the Electrochemical Society Meeting*, Buffalo, N. Y., pp. 52-53, October, 1957.
3. Technical Bulletin Abbey #100, Abbey Plastics Corp., Hudson, Mass.
4. Technical Bulletin 3-2-5B, Emerson & Cuming, Inc., Canton, Mass.
5. Technical Bulletin 3-2-5C, Emerson & Cuming, Inc., Canton, Mass.
6. Technical Bulletin 3-2-5A, Emerson & Cuming, Inc., Canton, Mass.
7. Technical Bulletin 3-2-5, Emerson & Cuming, Inc., Canton, Mass.
8. Bulletin #ECC-6250, Houghton Laboratories, Inc., Olean, N. Y.

RECENT DEVELOPMENTS IN PRINTED WIRING

SOLDER-PLATED CIRCUITS

The solder plating of printed wiring boards has become important at RCA because it seems to be the only way to get what has become known as "Boeing quality" solder dip coatings. (This term was popularized by Boeing Aircraft Co. where rigid specifications have been placed not only on the quality of soldered joints, to assure smooth, uniform, and strong junctions, but also on the quantity and appearance of the solder on the printed-circuit paths.)

Solder-plated circuits may be made in either of two ways, (1) the entire copper clad laminate can be solder plated before any other processing, or (2) only the circuit part can be plated, the noncircuit area being masked off by a resist.

The first method has an advantage. Plated boards are stored ahead of production use, so that the manufacturing process is not delayed by a relatively slow plating process. It has disadvantages however; these being difficulty of getting even thickness of solder plating over large areas, difficulty of plating exactly the composition of solder desired, and the necessity of using a silk-screen process (*Kodak Photo Resist, KPR*, does not adhere well to solder plate). Another problem is the undercutting of the resist to form a copper ledge approximately 0.005-inch wide on each side of the solder-plated circuit line. This under-

by

DR. O. D. BLACK

Materials Standards Section
Central Engineering
DEP, Camden, N. J.

cutting does not seem to be too objectionable when etching is carefully controlled, since this is adequately covered with solder in the subsequent solder-dipping.

The second method, that of solder plating only the desired circuit lines and areas, is the one used by the manufacturer producing the best-quality boards, so far. The entire copper area of the laminate is cleaned, then the photographic process is used to apply the *KPR* properly and leave bare, clean copper in the areas where the circuit paths are desired. Next, these areas are solder plated. The *KPR* is then removed, and the solder plate is used as a resist for etching away the unwanted copper areas. For the etching process, the Hunt Company's *Solder Circuit Etch* liquid is used in a splash-type etcher.

Both of these processes are undergoing tests here at the present time.

WATER-SOLUBLE FLUXES

Recently, water-soluble fluxes, which seem to offer a great deal of promise in dip-soldering applications for printed-

wiring boards, have been placed on the market. These fluxes may be hydrazine derivatives, such as hydrazine monohydrobromide. They are at least as active as *Kester 1571*, but enjoy the great advantage of being completely water-soluble. After their fluxing actions are complete, they decompose at molten-solder temperatures, leaving slight residues. These deposits are neither corrosive nor hygroscopic and wash away readily in a spray of warm water.

We have tested these fluxes and find no adverse effect on printed-wiring boards after one month at 95 percent relative humidity and 95°F, even when residues are left on the boards; however, as an appearance item, the boards should be washed after soldering. Two companies are supplying these fluxes: The Clinton Chemical Co., Santa Monica, California and the M. W. Dunton Co., Providence, Rhode Island. The Clinton material has been tested with highly favorable results, and the Dunton product is now undergoing pilot-plant checks in our Automation Group.

PAPER-EPOXY LAMINATES

Several manufacturers are offering flame-retardant paper-epoxy laminates with approximately the same electrical characteristics as the glass-epoxy laminates so extensively used in government work. This material has several desirable features, which should lead to wider use:

- 1) built-in flame retardance;
- 2) machines well at room temperature, and punches and shears better than any other electrical grade of laminate;
- 3) does not "age" appreciably or harden on further heating;
- 4) good moisture resistance of the order of glass epoxy;
- 5) high insulation resistance—as good as glass epoxy;
- 6) much cheaper than glass epoxy.

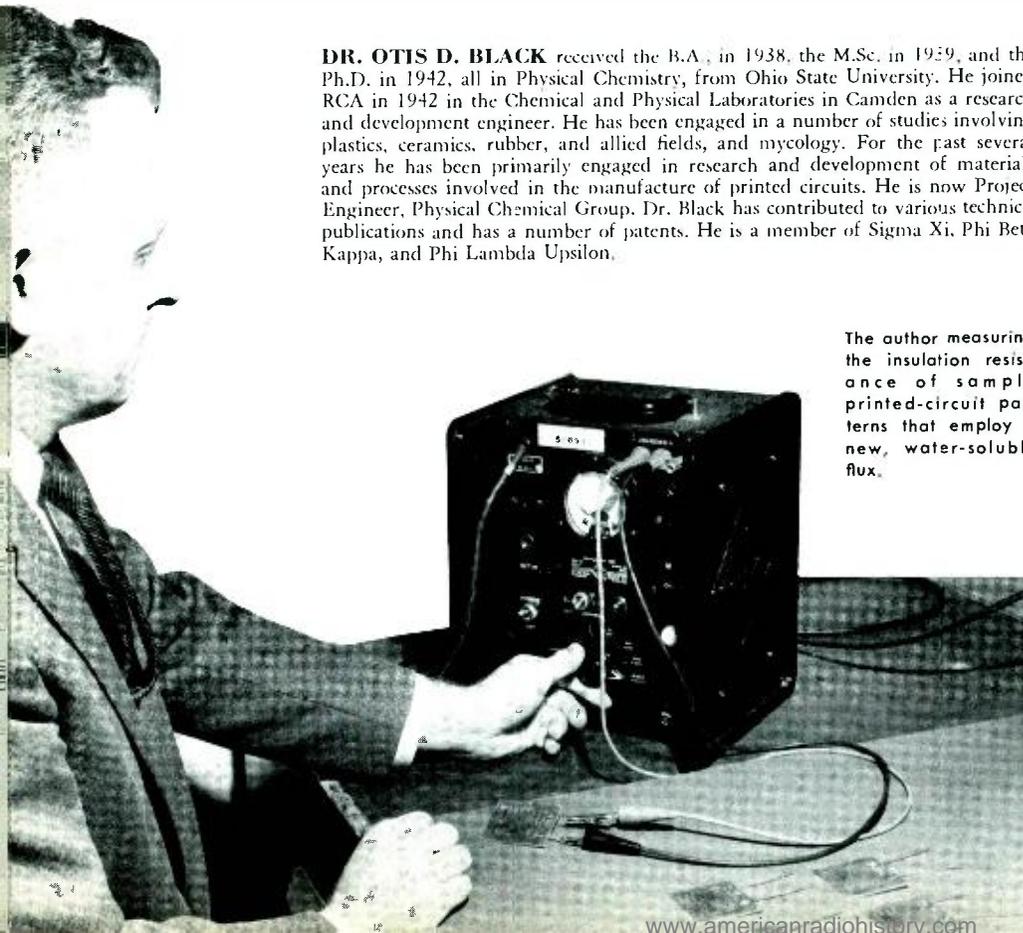
Below are approximate price relationships, based on 1-ounce copper, one side, and a 1/16-inch-thick laminate.

| Material | Price Per Square Foot |
|------------------|-----------------------|
| Paper phenolic | \$0.84 |
| Paper epoxy | 1.55 |
| G-10 Glass epoxy | 2.92 |
| G-11 Glass epoxy | 3.17 |

The paper-epoxy laminate has almost twice the flexural strength of paper-phenolic laminate, yet tests in the laboratory show that it is only slightly better in vibration and shock. Nevertheless, this should be more than compensated for by the other advantages of paper-epoxy reflected in the circuit design.

DR. OTIS D. BLACK received the B.A. in 1938, the M.Sc. in 1939, and the Ph.D. in 1942, all in Physical Chemistry, from Ohio State University. He joined RCA in 1942 in the Chemical and Physical Laboratories in Camden as a research and development engineer. He has been engaged in a number of studies involving plastics, ceramics, rubber, and allied fields, and mycology. For the past several years he has been primarily engaged in research and development of materials and processes involved in the manufacture of printed circuits. He is now Project Engineer, Physical Chemical Group. Dr. Black has contributed to various technical publications and has a number of patents. He is a member of Sigma Xi, Phi Beta Kappa, and Phi Lambda Upsilon.

The author measuring the insulation resistance of sample printed-circuit patterns that employ a new, water-soluble flux.



The present micromodule concept evolved from work performed at RCA during 1957-58. The initial concept then became a reality in 1958 through RCA work for the U. S. Signal Corps under Contract No. DA-36-039-SC-75968. RCA has continued as the technical and coordinating agency for the program, which has progressed industry-wide. In this article, Mr. Eddison reviews the wide range of micromodule materials, processes, and their associated problems. In the article that follows on P. 56, Dr. Schwartz and Dr. Stetson single out one of these topics — ceramics — for detailed discussion.

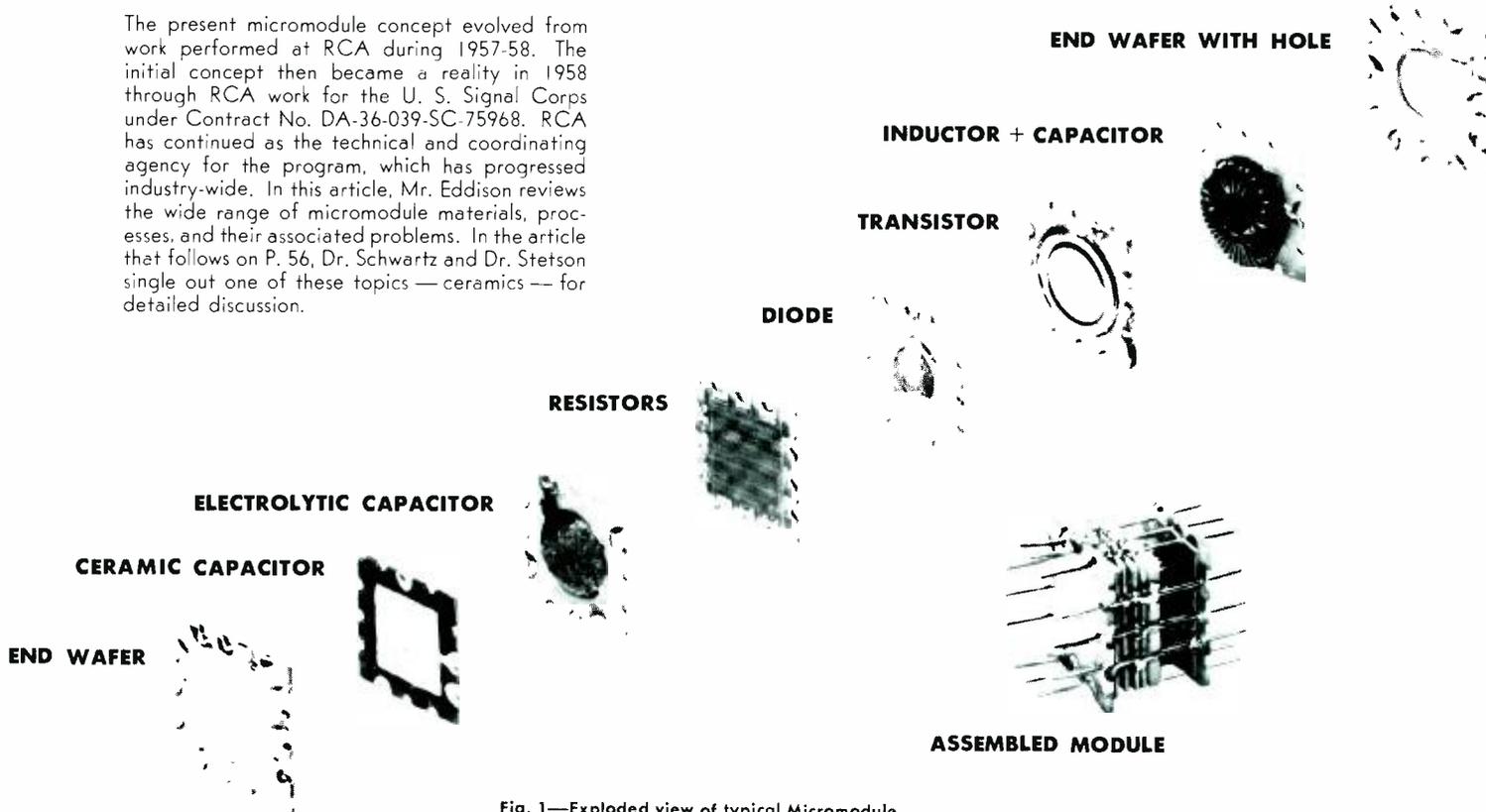


Fig. 1—Exploded view of typical Micromodule.

MATERIALS AND PROCESSES FOR THE MICROMODULE

THE GENERAL PURPOSES, characteristics, and design features of the micromodule have received wide publicity and are probably familiar to most RCA engineers. The chemical and physical means underlying the development of materials and processes by which the design was translated to a satisfactory product may not, however, be so well known.

Miniaturization invariably involves problems of both design and materials. Since the earliest concept of the micromodule, it was realized that material behavior would be a major factor in its development. Although none of the materials contemplated for use were new to science, it was recognized that the circuitry needs of the micromodule, and its small size and geometry, would create problems. Some of these needs were unusually small spacing between terminals, the requirements of mechanical strength in a construction of fragile elements, more-rigorous specifications for purchased components and materials, the severity of environmental specifications, and an indication of the need for modification of presently known materials in order to accomplish specific objectives. (Figs. 1 through 8 illustrate a typical micromodule, its components, and some of the processes and material involved. These will be discussed further in the article.)

by

C. EDDISON, Staff Engineer

*Micromodule Engineering
Semiconductor and Materials Division
Somerville, N. J.*

Because the dimensions and geometry for the micromodule had been specified from its earliest concept, and time and contractual obligations permitted no change, every effort was made to fit the existing capabilities of the component manufacturer into the material requirements of the module. Uniformity of shape, dimensions, and flatness—where flatness is important—were essential because automatic assembly was contemplated. It was soon discovered that although a number of manufacturers made excellent products, they were not necessarily acceptable for the micromodule. The reasons included such things as nonconformity to the required shape or dimensions, use of materials chemically different from those believed necessary for micromodule construction, some deviation from a required physical property, or failure to meet the extremely high reliability expectation under the storage, operating, life, and environmental conditions specified. Considerable work was necessary to satisfy, through materials and processes, the specifications for the prototype micromodule.

CERAMICS

The importance of ceramics in the micromodule cannot be exaggerated. Indeed, ceramics having different chemical and physical properties may be considered as the foundation around which the micromodule was developed. They serve as platforms or substrates on which other materials may be deposited to develop a component, as in the case of resistors; as supports for components, as in the case of inductors and dry electrolytic capacitors; as end wafers or "terminal boards"; and, because their dielectric values can be altered by modification of materials without jeopardy to other useful properties, may function as integral parts of the component, as in the case of high-*K* (dielectric constant) and precision capacitors. Without the appropriate ceramic of the right dimension, in the proper place, fulfilling a specific function, the development of the micromodule would have become an entirely different project.

The word *ceramic* does, of course, cover broad fields of application. This program, however, is concerned neither with window glass nor chinaware nor with such products of electrical ceramics as bushings, sockets, stand-off insulators, and the like. The ceramics used in the micromodule must meet many specific requirements. For example, the ceramic

substrate used as a platform for the deposition of other materials in resistor elements must have exceptionally high resistance itself, must have an extremely smooth, uniform surface, must provide adequate heat dissipation, must not be adversely affected by the material deposited on it, and must be chemically clean and free of ionizable material.

Measurements and experiments narrowed the choice of optimum nontoxic ceramic materials to specific kinds of glasses and aluminum oxide. Glasses, because of their extreme fragility in thicknesses of 10 mils. present more-severe manufacturing problems than aluminum oxide. The present choice for a resistor substrate is aluminum oxide, in spite of the fact that, because of its inherent porosity, it must be specially treated to present a smooth surface.

The end wafers and the substrates for dry electrolytic capacitors and inductors are generally less critical than ceramic parts for high-*K* and precision capacitors. The end wafers serve as "dams"

during the encapsulating process and, because all the riser wires are attached to them, also help provide mechanical strength. In addition, they afford means for making connections to other micro-modules or printed-circuit boards, and help provide means for heat dissipation. Because of the need for as much uniformity of material content as possible, aluminum oxide is also used for these wafers.

ELECTROLYTIC CAPACITORS

The requirement of small size in the micromodule spearheaded initial interest in the dry electrolytic capacitor. Probably the best known example of this type of capacitor is that using tantalum as the anode. The tantalum may be supplied as ribbon, coil, wire, or tape, or may be developed from a powder, by suitable pressing techniques, to the required dimension. If powder technology is used, a tantalum lead wire may be introduced simultaneously with the pressing operation, and the whole unit then be vacuum-sintered at a high temperature. This

technique provides considerable surface area. The next step anodizes the tantalum surface in a suitable electrolyte to an oxide of tantalum which is, of course, the actual dielectric medium. Care must be taken to ensure that the tantalum surface is constantly replenished with oxygen. Oxygen may be supplied by the use of a thin coating of manganese dioxide. A low-resistance contact to the anode is then provided. Carbon has been found to be a useful interface material for this purpose. The next process supplies the metallic cathode layer, usually silver, which may be applied by silk screening or an equivalent process.

Considerable progress has been made in this field and dry electrolytic capacitors filling all the requirements of the present micromodule have been developed.

PRECISION AND HIGH-K CAPACITORS

The field of improved high-*K* and precision capacitors presented a major challenge. The development of an improved



Fig. 2—Dry electrolytic capacitor in microelement form (rated up to 60 μ f-volts). The tantalum anode measures approximately 0.180 inch diameter and can be made from tantalum in various forms. Tantalum surface is oxidized to provide dielectric coating. A metallic cathode layer is applied by silk screening. Additional materials are used in making connections and terminations.

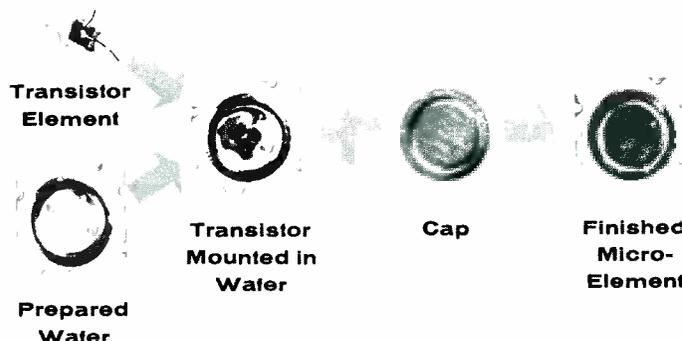


Fig. 3—Design and assembly of microelement transistors created problems in housings and hermetic seals. Different materials employed must be compatible and capable of withstanding production handling and heat application without adversely affecting performance.

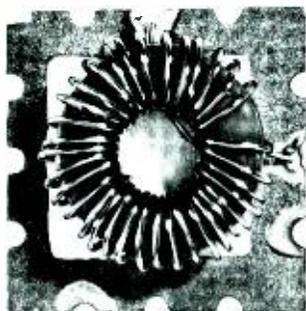


Fig. 4—Toroidal-wound inductor (for use to 80 mc up to 3-mh value) utilizes ferrite core and is mounted directly on a capacitor microelement to make a combination L-C circuit. Ferrite-core formulations and processing have required intensive investigation of materials and processing. The resulting core performance has been considerably in advance of the state of the art.

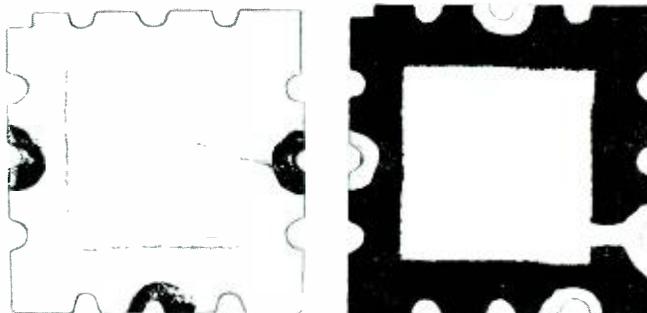


Fig. 5—Single-layer ceramic capacitors of 10-mil thickness and rated at 100 volts are made for precision (left, 5 to 30 μ f) and general-purpose (right, 100 to 6,000 μ f) applications. Various ceramic dielectric materials can be used in the wafers, upon which the capacitor electrodes are screened.

product requires chemical and physical arrangement of ceramic-like materials of defined particle size, with or without additives, under various processing conditions, in specific atmospheres, and at specific temperatures. Both rare-earth and the more common earth oxides were used to achieve the objective. In a typical formulation, barium and titanium oxides in specific ratios or molal compositions are combined through the agency of heat and in the presence of a small amount of ceramic flux to yield a material having dielectric constants or K values of 30 to 35 and Q values of 1000 to 2000. Lanthanum oxide may be similarly combined with titanium oxide to yield K values of 40 to 45 and Q values in excess of 10,000. The periodic table indicates the potential value of a number of oxides of different earth elements.

Composition, however, is not the only factor involved in the development of high- K or precision capacitor ceramics. Of equal, and perhaps more theoretical importance, is the study of ceramic materials structure.

RESISTORS

After a suitable ceramic substrate was selected, the problem of resistor development consisted of selecting materials and processes to meet the specified resistance values, tolerances, and reliability. It must be remembered that both the materials and processes used in manufacturing the various types of resistors presently used in the industry are very different, and the end results in terms of response to imposed specifications and reliability are not the same. A selective direction of effort was necessary to permit the most pertinent and economical returns.

Of the various resistor materials available, two seemed to offer the greatest immediate promise in terms of adaptability to the micromodule, chemical and physical properties, and reliability. These two materials are tin oxide, which is produced by spraying tin chloride, either with or without additives, on the heated substrate material, and thin metal films deposited on the substrate by vacuum techniques. Either method presents its special problems. If a resistor is developed from tin chloride, for example, the surface condition of the substrate, the temperature of the substrate at the time of spraying, the formulation of the tin chloride spray, the method of pattern development, and aging the completed resistor all exert their effect, individually or collectively, on such properties as ohms per square, final resistance, power dissipation, and temperature coefficient of resistance.

In the development of metal-film resis-

tors by vacuum deposition, the nature of the alloy evaporated and its freedom from contaminants are important considerations. Residual pressure at the time of evaporation is also important as is the method of pattern development. These and other factors control the properties of ohms per square, final resistance, power dissipation, and temperature coefficient of resistance.

The common denominators in the development of micromodule resistors by use of either tin chloride or metal films include selection of substrate material, its dimensions, its cleanliness, its smoothness of surface; its freedom from ionizable material; and aging of the final resistor and its protection from external environment. Such protection is provided by coatings and encapsulation.

TERMINATIONS

Each wafer of the micromodule is supplied with a number of terminations necessary for the performance of the component. The resistor employs twelve terminals to provide versatility of circuitry by freedom to select different resistance values. The end wafers also use twelve terminals for connection to other circuits.

Prior work had shown the wide adaptability of silver as a terminal or termination-pad material. Silver is easy to apply, is a good electrical conductor, and permits efficient soldering. Its use in the micromodule had to be re-evaluated, however, because of the number and extremely close juxtaposition of terminal pads (particularly in the case of resistors), the extreme environmental conditions to which the micromodule would be subjected, and the possibility of the introduction of traces of ionizable materials from any one of several potential sources. Silver migration had been experienced by others in critical application. If the same phenomenon occurred in the micromodule, severe restrictions would be placed on both its life and reliability.

Wafers were prepared with terminal pads of silver having the extremely small distances between them found in the micromodule. The wafers were then placed in a high-humidity cell under low voltage. Both electrical measurements and visual observation showed that silver migration did occur and that most protective films retarded, rather than eliminated, the difficulty. Consequently, the metal content of terminations became a subject of comprehensive investigation.

The metals and alloys used for experimental work in developing terminations, and also those used elsewhere in the micromodule, were watched closely for

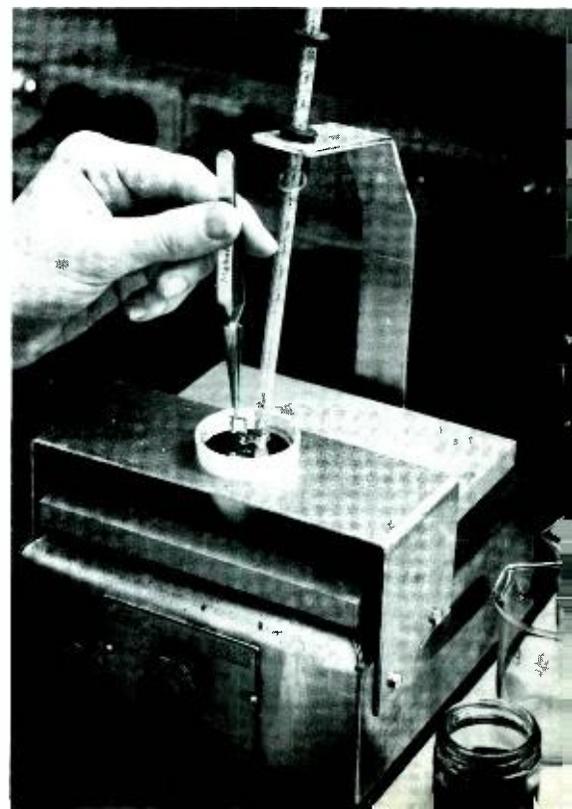
tendencies to develop metallic whiskers. An appropriate test system for such observation was developed. Only one case, that of electroplated tin on a riser wire, was noted. Electroplated tin in micromodule construction was subsequently eliminated.

Corollary investigation of the termination problem indicated the imperative need for unusual cleanliness. Solder fluxes, finger prints, and similar contaminants introduced ionizable material leading to breakdown. Materials for cleaning the micromodule after termination and immediately prior to encapsulation required isolation of particular solvents that would not chemically attack, or physically disturb, any of the parts or materials. Ultrasonic energy was found useful as part of the necessary processing. Because a number of components were externally purchased and their past history not totally known, care was essential to ensure that the characteristics of each component would be unimpaired by cleaning materials and processes.

INDUCTORS

Inductance is provided by a toroid-coil core construction. In most instances, the core is based largely on a ferrite using the oxides of iron and manganese, with small amounts of the oxide of nickel or copper, magnesium, and zinc. When such a core is heat-treated at a suitable temperature in an appropriate atmosphere, it provides values of permeability and Q

Fig. 6—Microelement terminations are coated with solder by dipping. Solder compositions, metallizing formulas and processes, and basic microelement materials must all be compatible to assure electrical performance and reliability.



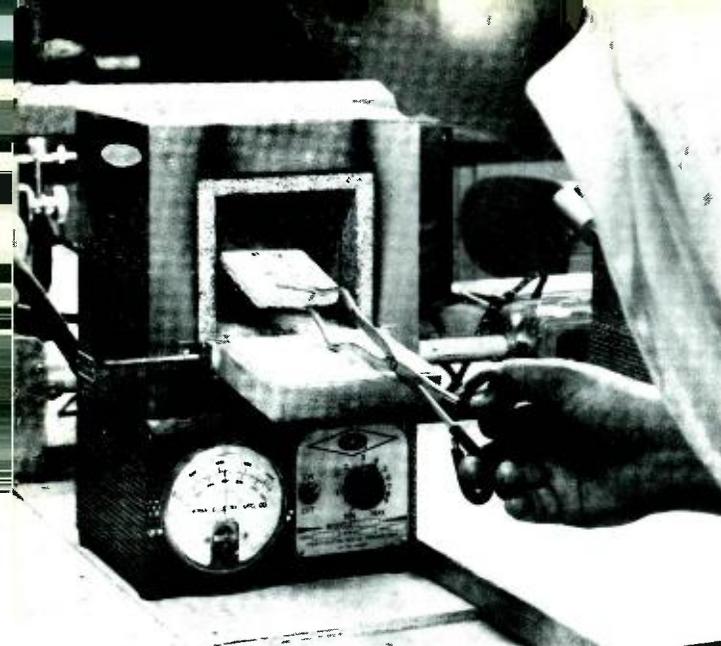


Fig. 7—Different firing processes are utilized in making various microelements. As successive firing operations are necessary in the process of completing many types of elements, the materials engineer must establish their qualities, limitations, and compatibility with each other and with various processes.

Fig. 8—Terminations are applied to a diode microelement by screening a silver paste onto the wafer through a 200-mesh stainless-steel screen. With the screening fixture shown here, four diode microelements can be screened simultaneously. The screened units are subsequently fired.



acceptable for most electronic applications. Because of the electrical requirements of the micromodule and the required temperature stability, a ferrite was developed using the oxide of nickel, modified by the introduction of extremely small quantities of carbon and the oxides of barium and molybdenum.

Because inductance is dependent on an insulated wire coil, the properties of the wire as well as the number of turns contribute to uniformity of inductance values. The properties of the conductor in the wire are important because copper purity, tensile strength, elongation, and yield point exert an appreciable effect on the end result. A conductor subject to undue tension may exceed its elongation value and cause breakage of the wire. A wire in tension beyond its yield point may be subject to breakage on the application of any further stress.

The insulation on the wire is also important in its chemical and physical properties. Physically, it may modify the properties of tensile strength and elongation. Chemically, it may react with solvents used in cleaning operations, with adhesives and impregnants used in making the substrate-coil-core assembly, or with the coating or encapsulant finally applied. Care was taken to ensure that the insulation would meet all the necessary conditions.

TRANSISTORS AND DIODES

Such a wealth of information is already available about transistors and diodes used in the micromodule that it would

be presumptuous to try to cover them here. However, a number of problems were met in their direct application to the micromodule. In particular, difficulties in housings and hermetic seals had to be overcome.

COATINGS AND ENCAPSULANTS

Coatings and encapsulants provide the means by which the micromodule is protected from specified environments. Coatings are applied locally to each component according to the need. They may be organic or inorganic in nature. They not only provide protection against abrasion and contamination of the component but also where organic materials are involved, contribute, by their compressibility, to a cushioning effect. Coatings must not react chemically with any material of any component and must not react adversely with the encapsulant.

Encapsulation is the last process in the making of the micromodule. A number of engineering considerations were recognized early in the work, among them a realization that the encapsulating material should not chemically react with any material used in the micromodule. It must be sufficiently flexible to eliminate any possibility of stress causing damage to fragile wafers, yet sufficiently rigid to maintain mechanical strength. The exotherm should be below a temperature which might cause damage to any component, but the softening point should be substantially above any temperature developed internally by the micromodule or any conceivable environ-

ment. Its electrical characteristics must be excellent, and it must maintain initial values over the expected life of the device. It must provide heat dissipation and guarantee that the Micromodule will meet military environmental and other specifications. Suitable coatings and encapsulants for the module have been developed.

Because of the small size of the micromodule and the presence of riser wires, special problems were encountered with respect to design of a mold for encapsulation. A number of materials were evaluated, including plastisols, silicone rubbers, and other polymers, to determine the optimum configuration and dimensions for final design and development of metal molds for future manufacturing purposes.

THE FUTURE

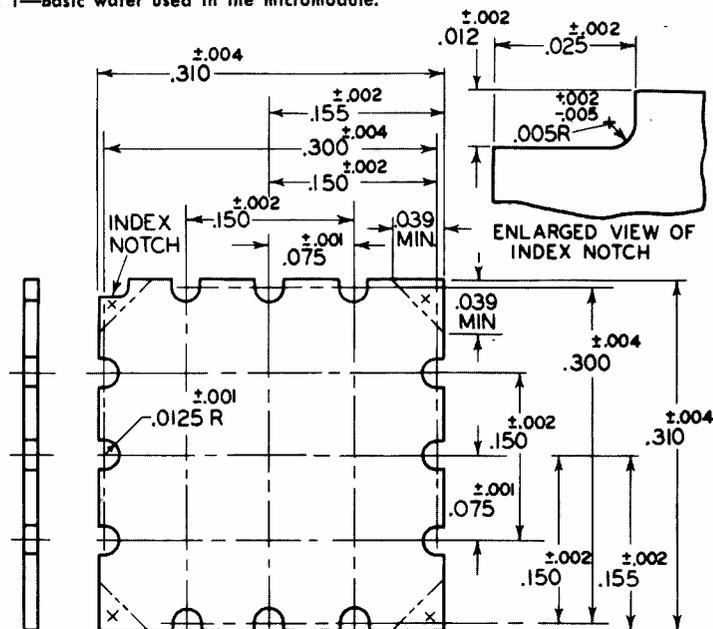
The development of the micromodule has presented many problems in the chemistry and physics of materials. The micromodule itself may be considered, perhaps, as at least one step between the use of materials for specific electronic devices in small mass and a product of the future where small mass will be replaced by minimum surface and a desired effect gained by a more informed control of the electron. New materials and material purity, difficult to visualize—and perhaps more difficult to obtain—may be required. Chemistry and physics will be equal to the problem and will contribute, as a force for progress, in our organization and in our industry.

C. EDDISON received the B.S. degree in Chemical Engineering from Leeds College of Technology. His experience includes six years with the Edison-Swan Electric Company in England as Chief Chemist, pioneer work on the therapeutic value of ultraviolet rays with Corning Glass Company and Cornell University, and photographic research with Ansco and the Bureau of Chemistry in Washington. He joined the Chemical and Physical Laboratory

of the RCA Electron Tube Division in Harrison in 1929, and became Manager of the Laboratory at Camden in 1941. In 1958, he transferred to the Semiconductor and Materials Division at Somerville as Staff Engineer in the Micromodule Engineering activity. Mr. Eddison is a member of the American Chemical Society, the National Society of Corrosion Engineers, and the American Electro-chemical Society.



Fig. 1—Basic wafer used in the micromodule.



CERAMICS AND THE MICROMODULE

by

Dr. B. SCHWARTZ and Dr. H. STETSON

Micromodule Engineering Ceramic Laboratories

Semiconductor and Materials Division

Somerville, N. J.

CERAMIC MATERIALS HAVE assumed an expanding role in this growing electronics era. The current trend toward miniaturization of electrical equipment has contributed to the exploitation of the solid-state properties of materials. There is an increasing tendency to replace vacuum tubes, air- and oil-dielectric capacitors, wire-wound resistors, and other components by smaller, solid-state devices. The micromodule program represents a major effort to achieve standardization of such devices so that the greatest advantages of miniaturization can be utilized in broad areas of electronic systems. This article reviews briefly the historical growth of electro-ceramics, reports the role that ceramics play in each of the micromodule elements, and points out areas for further research.

ELECTRO-CERAMICS

The field of ceramics may be considered to include all nonmetallic, inorganic materials which are heated to a high temperature as an integral part of their manufacture. Dinnerware, glassware, artware, and building materials such as brick, are common ceramic products. The new branch of electro-ceramics, which deals with the materials used in electrical devices, is an outgrowth of these earlier compositions.

As the electrical industry grew during the previous century, porcelain

(alkali aluminum silicate) and glass were used for high-voltage, low-frequency insulators. These materials are still in use because of their electrical and mechanical strength and resistance to the effects of moisture. In the present century, the use of higher frequencies in radio and radar required that insulators have lower dielectric loss and improved dimensional tolerances. Steatite ceramics (magnesium silicate) were developed and widely accepted for use in these precision parts.

Advances in electronics created a demand for materials with other new properties. The discovery of the high dielectric constant of titania was a major contribution to the manufacture of miniature capacitors.¹ Extensive research then followed on other titanates. The discovery of barium titanate, which has an extremely high dielectric constant and piezoelectric behavior, led to a wider use of ceramic capacitors and electro-mechanical devices.² Approximately half the capacitors made in this country today are of these types.

Another recent development was the replacement of glass envelopes in some vacuum tubes and transistors by envelopes of alumina and forsterite (magnesium orthosilicate).³ This change permits the devices to withstand higher temperatures and greater mechanical shock. The RCA Nuvistor is one prominent example. Reliable methods for

hermetically sealing ceramic to metal parts have also been developed and are now used in production.

Ferrites, which are magnetic ceramics, are also of great importance to the electronics industry. These materials are characterized by a very high electrical resistivity which makes them particularly valuable at high frequencies. (See *New Ferrites for Electronics*, this issue.)

THE MICROMODULE PROGRAM

The micromodule concept, structure, applications, and potentialities were described in detail in a previous issue of the *RCA ENGINEER*.⁴ (See also *Materials and Processes for the Micromodule*, this issue.) The principal initial objectives of the micromodule program include: (1) a ten-fold reduction in size and weight of existing electronic equipment; (2) improvement in maintenance through use of throw-away modules; (3) greater reliability as a result of fewer connections and improved technology; and (4) reduced equipment cost, through parts standardization and mechanized assembly.

Basic Wafer

The first step toward achieving these objectives was to establish a standard-size element or wafer, as shown in Fig. 1. Tolerances on this wafer are very close: ± 0.004 inch for length and width, ± 0.001 inch for thickness, and ± 0.001 inch for camber (warpage of the wafer). Control of camber, which is the most difficult of these requirements, is important because the spacing between microelements is only 0.010 inch. Such close spacings are necessary to obtain the desired packing density. Of the total space of 0.010 inch, 0.002 inch is reserved for the encapsulating material and 0.006 inch for build-up on element surfaces of resistors, capacitors, solder, and other materials. Therefore, a maximum of 0.002 inch is left for camber on two adjacent parts.

The economical manufacture of small ceramic parts to these tolerances requires special engineering effort. Because most ceramics are hard and abrasive, the use of conventional pressing methods causes dies to wear rapidly and changes the dimensions. In addition, linear shrinkages of as much as 10 to 18 percent occur when the ceramic wafers are sintered at temperatures up to 1750°C to vitrify them. Consequently, close control of every operation must be maintained to insure production of acceptable parts.

Some manufacturers are developing new methods in which the wafers are

punched from sheets of ceramic materials prior to sintering, instead of being individually pressed from powdered ingredients.⁵ Thus, the needs of the micromodule program are advancing the state of the art in some lines of ceramic manufacture.

Careful consideration is given to the selection of the ceramic materials for the wafer. Table I lists several possible materials and their representative properties. Alumina is presently being used for most elements, primarily because of its high strength and thermal conductivity. Other materials, such as steatite and special glasses, are being evaluated for selected parts.

The basic wafer serves as a substrate for resistors, transistors, and inductors. Whenever possible, however, the wafer is also used as a functioning part of the microelement. In the case of ceramic capacitors, for example, the wafer is made of the desired dielectric material.

Capacitors

Present ceramic-capacitor requirements of the micromodule program have been

example is a compound of zirconia with titania.⁶ A more complicated composition is barium pentatitanate, which X-ray studies showed to be a mixture of barium tetratitanate (positive coefficient) and titania. Most positive temperature coefficient materials having a high Q also have low dielectric constants. The zero-value compositions, therefore, also have low K values (about 20 to 45). Present high- K materials having a positive temperature coefficient have such a low Q that they cannot be used in blends for micromodule precision capacitors.

Until new zero temperature coefficient materials having higher K 's are developed, it is necessary to achieve the capacitance needed by the use of thinner dielectric layers. The capacitance C of a wafer (in micromicrofarads) is determined by the following equation:

$$C = \frac{0.224 KA}{t}$$

where K is the mean dielectric constant, A is the area of the electrode (square

tric constant rises very rapidly, as shown in Fig. 2. This sharp maximum can be lowered, broadened, or shifted with respect to temperature by additions of alkaline earth titanates, zirconates, and other oxides. In general, the higher the K , the greater is the temperature coefficient of the material. Although materials having a K of 10,000 are available, materials having a K of about 5000 are currently being used because they have better temperature characteristics. With such materials, equation (1) shows that a 0.010-inch wafer can provide about 5000 micromicrofarads of capacitance. Multilayer thin-film capacitors extend the range beyond the 300,000-micromicrofarad value needed. The Q of these capacitors is about 100.

Research at RCA is presently directed toward increasing the K of precision capacitors, improving the temperature coefficient of general-purpose capacitors, and extending the upper temperature limits of both types.

Resistors

Ceramics are used in micromodule resistors as the substrate for thin-film elements, such as tin oxide and evaporated metals. Although the substrate is known to influence the resistor's characteristics, it is difficult to specify the desired properties for the ceramic. Some general requirements are:

1. High electrical resistivity
2. Low dielectric loss
3. Good thermal-shock resistance
4. Minimum porosity
5. A uniformly smooth surface which is free from defects
6. Ability to maintain close dimensional tolerances
7. Thermal expansion coefficient compatible with that of the resistor film
8. Desirable hardness (sufficiently strong, but easily cut by a diamond wheel or sand-blasting).

These items are among the known significant factors. However, problems

TABLE I—Representative Properties of Ceramic Materials

| Property | Alumina | Steatite | Electrical | |
|--|----------------------|----------------------|----------------------|---------------------|
| | (96%) | | Porcelain | Forsterite |
| Dielectric Strength ($\frac{1}{4}$ " thickness at 25°C), volts/mil | 290 | 250 | 260 | 250 |
| Dielectric Constant (at 1 megacycle) | 9.0 | 5.6 | 6.1 | 6.5 |
| Volume Resistivity (at 25°C), ohms/cm ³ | >10 ¹⁴ | >10 ¹⁴ | >10 ¹⁴ | >10 ¹⁴ |
| Flexural Strength, psi | 45,000 | 20,000 | 12,000 | 20,000 |
| Thermal Conductivity, cal/sec/sq. cm/°C/cm | 0.055 | 0.008 | 0.005 | 0.009 |
| Hardness, Moh's Scale | 9 | 7.5 | 7.5 | 7.5 |
| Thermal Expansion per °C (20°C to 500°C) | 7.0x10 ⁻⁶ | 8.5x10 ⁻⁶ | 5.0x10 ⁻⁶ | 10x10 ⁻⁶ |
| Specific Gravity | 3.7 | 2.6 | 2.5 | 2.8 |

separated into two categories. Precision-type capacitors are required to have capacitance up to 2000 micromicrofarads, usually with zero temperature coefficient of capacitance, Q greater than 1000, and d-c voltage ratings of 50 to 100 volts. General-purpose capacitors are required to have capacitance up to 300,000 micromicrofarads, tolerances in the order of ± 20 percent and d-c voltage ratings of 50 to 100 volts.

The temperature coefficient and Q requirements of the precision capacitors are met by a group of ceramic dielectrics based on titania. The Rutile structure of titania has a mean dielectric constant (K) of about 115 and a negative temperature coefficient of capacitance. By means of reaction between titania and certain other oxides, materials having essentially a zero temperature coefficient can be obtained. One

inches), and t is the thickness of the dielectric (inches).

Thus, for a wafer having an electrode area of 0.2 inch by 0.2 inch, a thickness of 0.010 inch, and a K of about 30, the capacitance is about 30 micromicrofarads. If the wafer thickness is reduced to 0.001 inch, the capacitance of the device is increased to 300 micromicrofarads. The decreased thickness also makes it possible to use ten such layers in the same space, thus providing a maximum possible capacitance of about 3000 micromicrofarads. Multilayered capacitors having dielectric layers of 0.001 inch and less have been made in the laboratory.

General-purpose capacitors are usually made of modified barium titanate, which is a ferroelectric having a Curie point of 120°C. As this particular temperature is approached, the dielec-

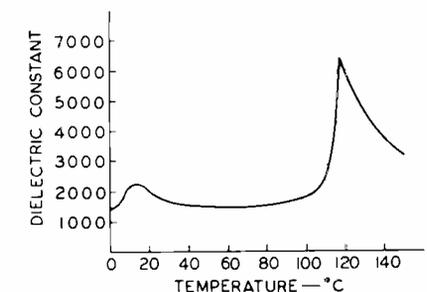


Fig. 2—Dielectric constant of barium titanate as a function of temperature.

still exist in defining and measuring the limits of each requirement. Item 5 is probably the most difficult to establish. Because the film thicknesses are in the order of 100 to 1000 angstroms, smoothness of the ceramic surface has to be controlled in the range of micro-inches. With these orders of dimensions, the crystal habits of the phases present in the ceramic become important. A glass surface is particularly good in this regard, but cannot always meet all the other requirements. "Free from defects" implies that there are no surface cracks, spots, pits, or blemishes. The requirement for high d-c resistivity of the ceramic is necessary to avoid shunting of the high-value resistor elements and to prevent electrolytic reactions in the ceramic which might be harmful to the resistance film. Hardness is important when the indicated cutting operations are used for lengthening the film resistance path.

Electrical porcelains of the clay, quartz, and feldspar type were among the first ceramics used for thin film resistor substrates.^{7,8} Alkali porcelains, however, are known to exhibit electrolytic polarization, which is detrimental to high-value resistors.⁹ As a solution to this problem, an alkaline earth porcelain was developed.¹⁰ Cordierite and similar bodies are usually too porous for use in resistors. Zircon porcelains have been reported as usable substrates,¹¹ but care should be taken to avoid a coarse-grain structure and iron spots. Some commercial metal-film resistors in current use employ steatite as a substrate, and tin-oxide film resistors are being made on glass. Alumina porcelain is also being studied extensively. Alumina has been tentatively selected as a substrate for micromodule resistors, but must still be evaluated fully. Future ceramic needs for resistors will lie in the region of improved homogeneity and surface structure, higher resistivity at elevated temperatures, and thermal conductivity.

Transistors

The micromodule transistor utilizes the ceramic wafer as a hermetic housing. In this application, the ceramic parts must be vacuum tight in thin sections (about 0.005 to 0.010 inch) and be capable of being metalized and sealed. Factors which affect vacuum tightness of ceramics have been reported in detail.¹² In general, diffusion of helium and larger gas molecules, such as water, through crystalline structures was reported impossible to measure.

Another important requirement of the ceramic is high thermal conductivity. The transistor is the most thermally

sensitive device of the elements discussed thus far. To control its performance, it is necessary to have good heat-removal design. Other desirable properties of the ceramic include good strength, ease of fabrication into intricate shapes, low dielectric loss, and high electrical resistance. Alumina is currently the principal choice, but several other materials are still being considered. *Fotoceram* (Corning Glass Works trade name) is attractive, particularly because of the advantages it offers in fabrication. Beryllia would be excellent because of its very high thermal conductivity, but it is toxic. Transistor design is in a period of change toward simpler construction and reliability in hermetic sealing.

SUMMARY

Ceramic materials play an integral role in each of the elements used to make a micromodule. The types of components now being used do not encompass all the electrical devices available for circuit design. Additional ceramics which may be used include thermistors, piezoelectrics, other types of ferrites and dielectrics, semiconductors, and insulators. Combinations of elements into a single wafer will be another trend in further miniaturization of electronic equipment. One example is the resistance-capacitance (RC) circuits now used commercially. These circuits utilize a resistance film which is deposited on a dielectric plate. This concept can be extended to RL and RCL circuits. Resistance and capacitance can also be built into the transistor wafer. Another improvement may be realized through more extensive use of ultra-thin evaporated and "sputtered" films, and junction zones within bulk materials which are controlled by diffusion.

It can also be expected that modules will be required to operate at higher temperatures in the future. Operation at these higher temperatures will further expand the need for ceramic.

To the ceramic technologist, the micromodule concept presents the opportunity to utilize the best developments in the electro-ceramic field and to create new materials and processes.

REFERENCES

1. E. Wainer, "High Titania Dielectrics," *Trans. Electrochem. Soc.* 89, 331-56 (1946).
2. A. Von Hippel, R. G. Breckenridge, F. G. Chesley, and L. Tisza, "High Dielectric Constant Ceramics," *Ind. Eng. Chem.*, 38, 1097-1109 (1946).
3. L. Navias, "Advances in Ceramics Related to Electronic Tube Developments," *J. Am. Ceram. Soc.* 37, 329-50 (1954).
4. O. B. Cunningham and B. V. Dale,

"The Micromodule," *RCA Engineer*, 4, 29-33 (1958).

5. Anon., *Ceramic Age* 73 (5), 36 May 1959.
6. W. Soyck, and A. Ungewiss, German Pat. 690,252 (March 28, 1940).
7. C. L. Snyder, "Specialized Ceramic Products—Their Use in German Communication Equipment," German Fiat Final Report No. 278, 3 Oct. 1945.
8. A. I. Miklashevski and R. I. Uspenskaya, "Porcelain Resistors," *J. of App. Chem. (U.S.S.R.)* 24 (3) 242-251 (1951).
9. M. D. Rigerink, "Ceramic Cores for Deposited Carbon Resistors," *Ceram. Age* (1) 10-13 (1954).
10. M. D. Rigerink and R. O. Grisdale, "Alkaline Earth Porcelains Possessing Low-Dielectric Loss," *J. Am. Ceram. Soc.*, 30 (3) 78-81 (1947).
11. I. Siegel and E. R. Olsen, Battelle Memorial Inst. "Designs for Pyrolytic-Carbon Resistors," Contract DA-36-039-sc-56615, First Quart. Rept., Nov. 15, 1953.
12. F. J. Norton, "Helium Diffusion Through Glass," *J. Am. Ceram. Soc.*, 36, 90-6 (1953).

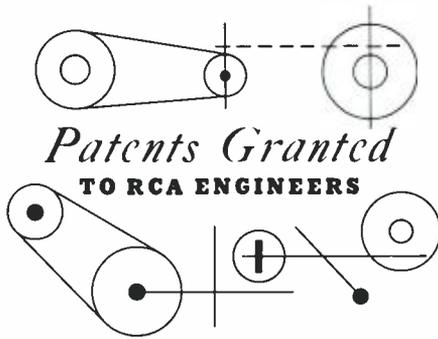


Dr. Schwartz

Dr. Stetson

DR. B. SCHWARTZ received the B.S. degree in Ceramic Engineering, Cum Laude, in 1948 from the New York State College of Ceramics at Alfred University. He received the degree of Sc.D in ceramics in 1951 from M.I.T. From 1944 to 1946, he worked on radar and radio equipment as a member of the Army Air Force. From 1948 to 1952, he was a member of the M.I.T. staff. From 1952 to 1954, he was Senior Ceramic Engineer for the Electronics Division of Sylvania Electric Products, Inc. From 1954 to 1955, he was Project Leader at Burroughs Corporation Research Center. From 1955-1958, he was Senior Research Ceramist at the International Resistance Co. He joined RCA in July of 1958 as Engineering Leader at the Semiconductor and Materials Division. Dr. Schwartz is active in the American Ceramic Society and is also a member of Sigma Xi Keramos, RESA, and IRE.

DR. H. W. STETSON, Ceramic Engineering, received the B.S. degree in Chemistry in 1950, the M.S. degree in Ceramics in 1952, and the Ph.D. degree in 1956, all from Pennsylvania State University. He was on the staff of the College of Mineral Industries from 1951 to 1955 as a full-time Research Assistant. From Glass Works as a Senior Ceramist. He worked on the study of ceramic-to-metal seals, low-thermal-expansion refractory ceramics, ceramic material and process development for radomes. He joined the Micromodule Product Development activity of the RCA Semiconductor and Materials Division in May of 1959. Dr. Stetson is a member of the American Chemical Society, the American Ceramic Society, the British Ceramic Society, Keramos, and Phi Lambda Upsilon.



Patents Granted TO RCA ENGINEERS

BASED ON SUMMARIES RECEIVED OVER A PERIOD OF ABOUT TWO MONTHS

DEFENSE ELECTRONIC PRODUCTS

Camden, N. J.

Information Handling Device

Pat. No. 2,877,446—granted Mar. 10, 1959 to A. D. Beard, I. H. Sublette, Moorestown, and L. C. Hobbs and S. M. Fillebrown, no longer with RCA.

Apparatus for and Method of Counting Perturbations in a Field

Pat. No. 2,907,519—granted Oct. 6, 1959 to F. D. Covely, 3rd.

Automatic Programmed Delivery System

Pat. No. 2,891,654—granted June 23, 1959 to D. E. Townsend, and M. Kaplan, no longer with RCA.

Method of Etching Copper

Pat. No. 2,908,557—granted Oct. 13, 1959 to O. D. Black and L. H. Cutler.

Magnetic Recording Reproducing

Pat. No. 2,908,770—granted Oct. 13, 1959 to H. R. Warren.

Message Spacing Control System

Pat. No. 2,907,002—granted Sept. 29, 1959 to J. N. Smith, and W. R. Ayres no longer with RCA.

Punched Card Operated Apparatus

Pat. No. 2,903,529—granted Sept. 8, 1959 to H. F. Hanthorn.

Semi-Conductor Squelch Circuit

Pat. No. 2,904,678—granted Sept. 15, 1959 to M. E. Malchow.

Selective Indicia Production

Pat. No. 2,907,018—granted Sept. 29, 1959 to L. E. Haining.

Digital-To-Analogue Converter

Pat. No. 2,907,021—granted Sept. 29, 1959 to W. E. Woods.

Turret Lens Indexing and Focusing Apparatus

Pat. No. 2,905,069—granted Sept. 22, 1959 to J. J. Ayres, and C. T. Cole, Jr., IEP, Camden.

Power Supply

Pat. No. 2,905,881—granted Sept. 22, 1959 to S. Aron.

Moorestown, N. J.

Power Supply

Pat. No. 2,903,638—granted Sept. 8, 1959 to L. L. Evans and D. F. Sprengeler.

Information Handling Device

Pat. No. 2,877,446—granted Mar. 10, 1959 to I. H. Sublette, A. D. Beard, Camden, and L. C. Hobbs and S. M. Fillebrown no longer with RCA.

Burlington, Mass.

Magnetic Storage Systems

Pat. No. 2,911,629—granted Nov. 3, 1959 to H. J. Wetzstein and Z. K. Kawecky.

Magnetic Storage System

Pat. No. 2,911,630—granted Nov. 3, 1959 to E. E. Dinowitz.

INDUSTRIAL ELECTRONIC PRODUCTS

Camden, N. J.

Turret Lens Indexing and Focusing Apparatus

Pat. No. 2,905,069—granted Sept. 22, 1959 to C. T. Cole, Jr., and J. J. Ayres, DEP Camden.

Secrecy Systems

Pat. No. 2,905,747—granted Sept. 22, 1959 to M. C. Kidd, and J. J. Davidson, H. I. Cherry Hill.

Television Receiver Signal Processing Circuits

Pat. No. 2,906,817—granted Sept. 29, 1959 to M. C. Kidd, and H. C. Goodrich, H. I. Cherry Hill.

Monitoring Circuits

Pat. No. 2,904,781—granted Sept. 15, 1959 to A. Katz.

Automatic Inspection Apparatus

Pat. No. 2,905,318—granted Sept. 22, 1959 to R. E. Schell.

System to Control Inter-Message Spacing

Pat. No. 2,907,010—granted Sept. 29, 1959 to A. M. Spielberg, H. P. Guerber, and L. C. Hobbs no longer with RCA.

Signal Statcizer

Pat. No. 2,907,989—granted Oct. 6, 1959 to H. P. Guerber.

Relaxation Oscillating Circuit Arrangement

Pat. No. 2,907,919—granted Oct. 6, 1959 to R. W. Sonnenfeldt.

Indexing Device

Pat. No. 2,906,200—granted Sept. 29, 1959 to F. W. Pfefer.

Information Translating System

Pat. No. 2,902,679—granted Sept. 1, 1959 to W. J. DePhillipo, and K. L. Chien no longer with RCA.

Control System

Pat. No. 2,902,687—granted Sept. 1, 1959 to A. J. Grange.

Automatic Phase Equalizer

Pat. No. 2,906,866—granted Sept. 29, 1959 to L. E. Thompson.

Time or Phase Measuring System

Pat. No. 2,906,946—granted Sept. 29, 1959 to R. W. Sonnenfeldt.

Signal Wave Analyzer

Pat. No. 2,906,947—granted Sept. 29, 1959 to R. A. Dischert and R. G. Thomas.

Color-Correction Systems

Pat. No. 2,902,539—granted Sept. 1, 1959 to L. Shapiro.

HOME INSTRUMENTS

Cherry Hill, N. J.

Secrecy Systems

Pat. No. 2,905,747—granted Sept. 22, 1959 to J. J. Davidson, and M. C. Kidd, IEP Camden.

Signal Operated Automatic Color-Killer System

Pat. No. 2,906,814—granted Sept. 29, 1959 to L. Dietch.

Television Receiver Signal Processing Circuits

Pat. No. 2,906,817—granted Sept. 29, 1959 to H. C. Goodrich, and M. C. Kidd, IEP Camden.

Transistor Phase Detector Circuit

Pat. No. 2,906,818—granted Sept. 29, 1959 to H. C. Goodrich.

Tuned Amplifier Neutralization System

Pat. No. 2,902,546—granted Sept. 1, 1959 to L. A. Horowitz and G. G. Hermeling.

Multi-Beam Convergence System

Pat. No. 2,903,622—granted Sept. 8, 1959 to J. C. Schopp.

Transistor, Operating in Collector Saturation

Carriers-Storage Region, Converting Pulse Amplitude to Pulse Duration
Pat. No. 2,905,815—granted Sept. 22, 1959 to H. C. Goodrich.

Combined Synchronous Demodulator and Brightness Signal Channel

Pat. No. 2,908,751—granted Oct. 13, 1959 to R. K. Lockhart.

Color Signal Demodulating and Matrixing

Pat. No. 2,908,752—granted Oct. 13, 1959 to R. K. Lockhart.

WEB Reeling System

Pat. No. 2,908,495—granted Oct. 13, 1959 to D. R. Andrews, and E. A. Bird no longer with RCA.

ELECTRON TUBE DIVISION

Harrison, N. J.

Pneumatic Detecting and Sorting Apparatus

Pat. No. 2,902,149—granted Sept. 1, 1959 to H. L. Blust, H. A. Strych, and G. Vivian.

Matching Device

Pat. No. 2,901,712—granted Aug. 25, 1959 to A. G. Hogg.

Lancaster, Pa.

Method of Aluminizing Phosphor Screens

Pat. No. 2,910,376—granted Oct. 27, 1959 to J. A. Stankey and M. N. Slater.

Coating Apparatus

Pat. No. 2,902,973—granted Sept. 8, 1959 to M. Weingarten, F. D'Augustine, and G. R. Bange.

Method of Applying Films to Cathode Ray Tube Screens

Pat. No. 2,903,377—granted Sept. 8, 1959 to T. A. Saulnier.

Positive Ion Trap Gun

Pat. No. 2,903,612—granted Sept. 8, 1959 to D. D. VanOrmer.

Sintered Photoconducting Photocells and Methods of Making Them

Pat. No. 2,908,594—granted Oct. 13, 1959 to G. S. Briggs.

Electron Tube

Pat. No. 2,909,698—granted Oct. 20, 1959 to L. P. Garner.

Zinc Sulfide-Coated Phosphor Partides, Phosphor Screen, and Method of Making Screen

Pat. No. 2,908,588—granted Oct. 13, 1959 to S. A. Harper.

ASTRO-ELECTRONIC PRODUCTS

Princeton, N. J.

Class B Transistor Amplifier

Pat. No. 2,892,045—granted June 23, 1959 to A. I. Aronson.

NATIONAL BROADCASTING CO.

New York, N. Y.

Audience Survey System

Pat. No. 2,903,508—granted Sept. 8, 1959 to J. L. Hathaway.

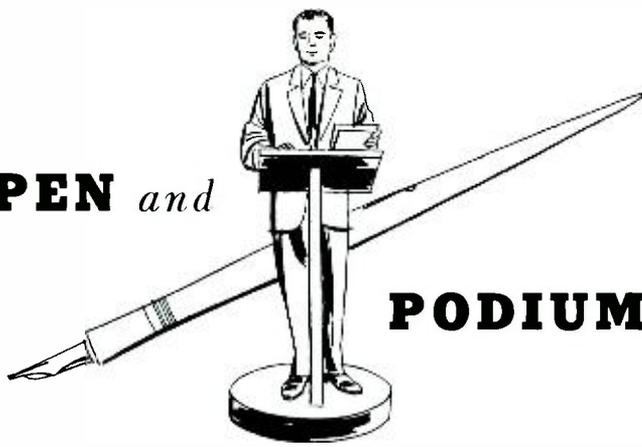
RCA SERVICE CO.

Cherry Hill, N. J.

Semiconductor Power Devices and Method of Manufacture

Pat. No. 2,905,873—granted Sept. 22, 1959 to J. Ollendorf, and J. Bibby no longer with RCA.

PEN and



PODIUM

BASED ON REPORTS RECEIVED OVER A PERIOD OF ABOUT TWO MONTHS

DEFENSE ELECTRONIC PRODUCTS

Camden, N. J.

Parametric Recognition of Phonetic Sound

By W. F. Meeker: Seminar on Speech Compression and Processing, AFCRC, Bedford, Mass., Sept. 30, 1959. Parametric speech bandwidth compression systems in which formant frequencies, formant amplitudes, pitch, and voiced-unvoiced distinctions are transmitted and used at the receiver to synthesize speech, have achieved a considerable degree of intelligibility. This presentation discusses the validity of this approach for speech recognition.

Test Equipment Standardization

By H. S. Ingrahm: Administration, and advantages of DEP program. Nov. 13, 1959, Annual Electronic Engineering Representatives Show, Philadelphia, Pa.

Experimental Verification of Reliability

By M. P. Feyerherm: Nov. 17, 1959, Reliability and Components Lecture Series, Montclair, N.J. Preparations and factors to be considered in testing electronic equipment for the verification of its reliability and the interpretation of the test data.

Design of a Wire Communication System in a Shielded Passageway of the BMEWS Radar Systems

By H. G. Schwarz: Oct. 7, 1959, in Chicago. Preventive measures in planning stage of a large radar system to minimize interference on communication links.

Moorestown, N. J.

Loaded Q of Transmission Line Tank Circuits

By R. A. Henderson: Sept. 18 issue, *Electronics*. The equation for Q is so arranged that the greater part can be plotted as a function of live length. Then Q is obtained by multiplying this part by the ratio of loop impedance to live impedance.

INDUSTRIAL ELECTRONIC PRODUCTS

Camden, N. J.

An Automatic Sensitivity Control for Monochrome Film Cameras

By H. N. Kozanowski, S. L. Bendell, and K. Sadashige: Oct. 8, 1959, SMPTE 86th Convention, New York City. A device for automatic control of signals levels from vidicon camera chains to accommodate unpredictable variations in average density of films used in TV programming.

A Magnetic Disc Recording and Reproducing System for Broadcast Applications

By G. A. Singer: SMPTE Convention, New York, Oct. 5, 1959. Pre-grooved disks, molded from a dispersion of iron oxide in an elastomer over an aluminum cover which combine the advantages of magnetic recording with the handling ease of disks. A specially designed narrow track head which rides in the groove is used for both recording and reproducing.

New Equipment for Measuring Envelope Delay

By E. N. Luddy: Annual Symposium, Professional Group on Broadcasting, IRE, Sept. 25-26, 1959, Washington, D.C. Effects of envelope delay distortion in TV systems, and improvements by proper equalization and the RCA BW-8A Envelope Delay Measuring Set, being introduced for TV station use.

A Transport Mechanism Design for the Television Tape Recorder

By J. G. Lee: Oct. 9, 1959, SMPTE 86th Semiannual Convention, New York City. Major units of a TV tape transport mechanism; basic function performed by each and its relation to the complete system.

The RCA 501 System

By J. A. Brustman: Eighth Annual Industrial Electronics Symposium, Pittsburgh, Pa., Oct. 1, 1959. Design technique in the input-output area of the RCA 501 EDP System and features of the new RCA 502 and 504 Computers.

RCA's Automatic Message Switching Center

By T. L. Genetta, J. L. Owings, and J. F. Page: Oct. 13, 1959, NEC, Chicago. RCA's AUTODATA, a fully automatic, completely transistorized message switching center which assimilates the large flow of traffic in large communication networks.

Progress in the Development of Electronic Vehicle Detection

By C. O. Caulton: Annual Meeting for the Electronic Committee of the American Assn. of State Highway Officials, Boston, Mass. RCA Electronic Vehicle Detector, resulting from original work by the David Sarnoff Research Center in the field of the control of vehicles on highways and a subsequent contract for the Federal Aviation Authority to detect and route all types of vehicles on the ground at airports.

Selection of Air Filters for Electronic Equipment

By T. G. Nessler: Aug., 1959 *Electrical Manufacturing*, a comprehensive guide for selection and application of air cleaning devices used in electronic equipment.

Millimicrosecond Diode Capacitor Memory

By M. M. Kaufman: Oct. 12, 1959, NEC Conference, Chicago. In 1953, the NBS built a diode capacitor memory of 10,000 bits with a ten microsecond cycle time using junction types having a basic speed limitation because of minority carrier storage and diffusion time. This technique has been studied and a prototype memory built using faster diodes to evaluate difficulties in reducing cycle time to approximately 10 millimicroseconds.

Servomechanisms in the RCA Television Tape Recorder

By J. W. Wentworth: Published by the Broadcast and TV Division. Fundamentals of servomechanism design and detailed descriptions of the three servo systems used in the TV tape recorder. First installment of

a training manual covering the operation and parts of the RCA TRT-1A/1AC TV Tape Recorder, completion of which is anticipated early in 1960.

Compatible Color Television

By J. W. Wentworth: A popular lecture presented to a group of high-school teachers concerning a semi-technical derivation of the color TV transmission standards, basic principles of colorimetry, and several electronic techniques used for encoding and decoding color TV signals.

ELECTRON TUBE DIVISION

Harrison, N. J.

Voltage Control of Magnetron Frequency

By C. L. Cuccia: *Electronics*, July 10, 1959. A new type of crossed-field device, the reflex magnetron, which permits control of the frequency of the magnetron as a function of the magnetron current.

Miniaturized Low-Noise Traveling-Wave Tubes for Airborne Applications

By C. L. Cuccia, H. J. Wolkstein, and J. J. Napoleon: IRE WESTCON Convention, Los Angeles, Calif., Aug. 18-21, 1959, and published in the *IRE WESTCON Convention Record*, August, 1959. This paper describes developmental L- and S-band traveling-wave tubes suitable for use in the input stages of octave-bandwidth traveling-wave-tube chains in airborne equipment.

Role of Powder Density in Dry-Pressed Ceramic Parts

By W. C. Allen, T. F. Berry, and W. A. Hassett: *American Ceramic Society Bulletin*, Aug., 1959. Effects on pressed and fired steatites of the properties of the powdered raw materials.

The Effect of Flux Distribution on Iron Losses

By M. J. Schindler: AIEE Fall General Meeting, Chicago, Oct. 12, 1959. Attempts to determine approximate solutions for Maxwell's field equations under the condition of variable permeability that will lead to a modified formula for determining eddy-current losses in magnetic sheet steel.

An Electrostatically Focused Traveling-Wave Tube for Wide-Band Amplification in L- and S-Band

By C. L. Cuccia and W. C. Johnson: NEC Conference, Chicago Oct. 14, 1959, an electrostatically focused traveling-wave tube designed for use in systems requiring wide-band amplification at a power level of 5 watts in L-band and S-band.

A Family of Medium-Noise Periodic-Permanent-Magnet-Focused Traveling-Wave Tubes

By G. Hodowanec, W. Poelstra, and J. Nelson: IRE Electron Devices Meeting, Washington, D.C., Oct. 29, 30, 1959. Traveling-wave tubes of the periodic-permanent-magnet-focused type having octave coverage at L, S, and C bands and noise figures of the order of 12 to 16 db. Design features which permit tube operation under severe environmental conditions.

Status Report on the Environmentalization of Traveling-Wave Tubes

By J. S. Posner: IRE Electron Devices Meeting, Washington, D.C. Oct. 29-30, 1959. Novel design approaches to some of the major factors which could severely limit traveling-wave-tube performance, including ambient air temperatures, mechanical vibration, and layout.

Lancaster, Pa.

Surplus Searchlight Makes Solar Furnace
By P. G. Herold: *Chemical Engineering*, June 1, 1959. Construction of a solar furnace used in investigations of various high-melting-point compounds and metal-and-oxide combinations to determine their suitability for use in tube construction.

Sensitivity and Motion-Capturing Ability of Television Camera Tubes
By R. G. Neuhauser: July, 1959 *SMPTE Journal*. Determines the sensitivities of various camera tubes in terms of the illumination levels required for both standard and non-standard TV scanning rates.

Color Tube Design: A Report on the State of the Art
By H. C. Moodey: IRE Emporium Section Seminar, Aug. 28, 1959, Emporium, Pa. Compares a number of important features of several types of color TV reproducers. Reasons for RCA's choice of the shadow-mask system.

For 5SB Service: Cathode-Driven Linear Amplifier using RCA-7094 Beam Power Tube
By C. E. Doner: August *RCA Ham Tips*. Extremely stable, five-band, cathode-driven linear amplifier for single-sideband service.

Evolution and Absorption of Bases in Electron Tubes
By J. C. Turnbull and R. H. Collins: Dr. A. H. Sommer of Princeton Laboratories made this presentation at the Internat'l Symposium on Residual Gases in Electron Tubes in Como, Italy, Sept. 23, describing the determination of gas-evolution effects in vacuum tubes and the speed of absorption of the 21CYP22 color picture tube for various gases.

Ultra-High-Vacuum System Developments for the Model C-Stellarator
By J. T. Mark and K. Dreyer: American Vacuum Society Symposium, Philadelphia, Oct. 7-9. Ultra-high-vacuum system being designed for C-Stellarator.

Evaluation of Large Diffusion Pumps and Traps for the Ultra-High-Vacuum System of the Model C-Stellarator
By W. G. Henderson, J. T. Mark, and C. S. Geiger: American Vacuum Society Symposium, Philadelphia, Oct. 7-9. Pumps, traps, and pressure gauges chosen for use on the C-Stellarator, and operating procedures necessary to maintain ultra-high vacuum in a continuously pumped system.

Ceramic, Sapphire and Glass Seals for the C-Stellarator
By I. E. Martin, J. A. Zollman, and J. A. Powell: ACS Electronics Division Fall Meeting, Philadelphia, Sept. 23, and American Vacuum Society Symposium, Oct. 7-9. Development and use of seals with the C-Stellarator.

Sintered Cadmium-Sulfide Photoconductive Cells
By C. P. Hadley and E. Fischer. NEC Conference, Chicago, October 12-14. Properties of sintered CdS photoconductive cells, and fabrication techniques.

Solid-State Image Intensifier Under Dynamic Operations
By C. P. Hadley and R. W. Christensen. IRE Electron Devices Meeting, Washington, D.C. October 29-30. Experimental and theoretical analyses of time-delay phenomena exhibited by solid-state image intensifiers of the photoconductor — electroluminescent-phosphor type.

Princeton, N. J.

RF Interaction Theory for an Electrostatically Focused High-Power Traveling-Wave Tube
By W. W. Siekanowicz. Electron Tube Research Conference, Mexico City, June, 1959. A theory of small-signal rf interaction between an electron beam having a periodically varying dc velocity and a traveling-wave-type circuit.

Microwave Parametric Subharmonic Oscillators For Digital Computing
By F. Sterzer. *Proceedings of the IRE*, Aug., 1959. A variable-capacitance subharmonic oscillator having an output frequency of 2000 megacycles and its use in circuits for amplifying, scaling and performing logic functions.

An Electrostatically Focused High-Power Traveling-Wave Tube
By E. F. Belohoubek, W. W. Siekanowicz, and F. E. Vaccaro. IRE Electron Devices Meeting, Washington, Oct. 29-30. Design and performance characteristics of a recently developed, high-power, X-band, electrostatically focused traveling-wave tube which uses an rf structure other than bifilar helices to obtain considerably higher power output and frequency than earlier tubes of this type.

SEMICONDUCTOR AND MATERIALS

Somerville, N. J.

Investigation of the Electrochemical Characteristics of Organic Compounds: Part V—Heterocyclic Nitro Compounds
By R. Blinksman and C. K. Morehouse: Electrochemical Society Meeting, Columbus, Ohio, Oct. 18-22, 1959. Electrochemical characteristics of heterocyclic nitro compounds and their use as cathodes in primary cells.

Investigation of the Electrochemical Characteristics of Organic Compounds: Part VI—Aromatic Hydroxy, Aromatic Amine and Aminophenol Compounds
By R. Glicksman: Electrochemical Society Meeting, Columbus, Ohio, Oct. 18-22. Electrochemical characteristics of organic reducing agents and the effect of added groups, aromaticity and electrolyte pH on their anode potential.

Magnesium Primary Cells with Perchlorate Electrolytes
By G. S. Lozier and C. K. Morehouse. Electrochemical Society Meeting, Columbus, Oct. 18-22. Desirable properties of magnesium perchlorate for use as an electrolyte in magnesium primary cells.

Minute Resistivity Variations in Germanium Crystals—Their Detection and Their Effect on Devices
By G. Meltzer: Electrochemical Society Meeting, Columbus, Ohio, Oct. 18-22. Development of two methods of detecting minute resistivity variations and their correlation to provide full information quantitatively and qualitatively.

A High-Power, High-Voltage, Diffused Germanium Transistor
By D. R. Carley. Washington, D.C. October 29-30, IRE Electron Devices Meeting. High-power, high-voltage germanium transistor which uses solid-state diffusion to form the emitter and collector junctions.

Gallium-Arsenide High-Temperature Diodes
By A. J. Wheeler and L. D. Armstrong. IRE Electron Devices Meeting, Washington, D.C. October 29-30. Techniques used to fabricate gallium-arsenide diffused-junction diodes and related problems.

Investigation of the Electrochemical Characteristics of Organic Compounds: Part IV—Quinone Compounds
By R. Glicksman and C. K. Morehouse: Effect of such factor as group substitution, aromaticity, and pH on the operating potential and coulombic capacity of various quinone compounds.

Transistorizing Automobile Broadcast Receivers
By R. A. Santilli and C. F. Wheatley: *Electronics*, Sept. 18. A five-transistor automobile receiver designed to use newly developed economical RCA drift transistors.

Design of Transistorized DC-to-DC Converters
By C. R. Turner: *Electronic Design*, Sept. 16 and 30, 1959. All the necessary data for the design of transistorized ringing-choke and transformer coupled dc-dc converters.

Ultra-High-Vacuum Pumping by Vibrating Membrane
By H. J. Schwarz: American Vacuum Society Symposium, Philadelphia, October 7-9. A new type of noncontaminating ultra-high-vacuum pump in which a diaphragm or membrane is driven into high-frequency vibration so that gas molecules are driven selectively in a perpendicular direction to the diaphragm surface.

The Micromodule: A New Approach to Electronic Packaging
By D. Mackey: N. J. IRE Section Meeting, Montclair, N.J., Oct. 14, 1959. History of the Micromodule program; concept, geometry and efficiency.

Infrared Studies of Birefringence in Silicon
By S. Lederhandler: *Journal of Applied Physics*, Oct. 1959, covering the study of permanent and elastic strains in silicon by observation of the crystal birefringence.

Needham, Mass.

Thermoelectric Properties of Some Mixed Oxides
By R. A. Horne, H. Lesoff, and Y. Kersey: *Journal of Chemical Physics*, Oct. 1959. Temperature dependence of the Seebeck coefficients ("Thermoelectric power") and the electrical resistivities of some mixed oxide materials.

ASTRO-ELECTRONIC PRODUCTS

Princeton, N. J.

Bibliography of Digital Magnetic Circuits and Materials
By W. L. Morgan: Sept. 1959 in *Proceedings of the IRE*. A list of approximately 400 references relating to magnetic memory and logic circuits divided into 19 sections.

RCA SERVICE CO.

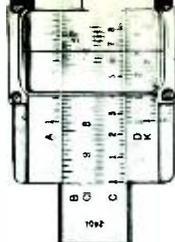
Cherry Hill, N. J.

Some Product "Abilities" Important to the Customer
By J. A. Cafaro: 13th New England Quality Control Conference, Providence, R. I., November 4-6. Recognition, measurement and specification of a number of product "abilities" instrumental in obtaining full customer satisfaction.

NATIONAL BROADCASTING CO.

New York, N. Y.

A Special Effects Amplifier for Non-Composite or Composite, Monochrome or Color TV Signals
By R. Kennedy: Oct. 8, 1959, SMPTE Conference, New York. A switching circuit has been designed to produce a doublet impulse transition of 0.05 microseconds. A method of clamping a color signal during the burst interval with crystal diodes is presented. Nonlinear amplification of the switching data prior to regenerative clipping permits dependable switching with much smaller brightness changes.



WENTWORTH WINS HONORABLE MENTION IN ETA KAPPA NU AWARD



John W. Wentworth has been named for honorable mention in the Eta Kappa Nu Recognition of outstanding young electronic engineers for 1959. In capturing this coveted honor, John Wentworth has established an enviable record among engineers throughout the electronics industry.

His accomplishments are so numerous and outstanding that they would be the subject of a separate article and unfortunately cannot be treated in the limited space provided here. John's professional experience began in July 1949 when he became a specialist trainee with RCA in Camden—following his graduation from the University of Maine with one of the highest scholastic grades of the university, where he was valedictorian of his class and a member of three honorary societies.

In January 1950 John was given a permanent assignment in Broadcast Studio Engineering and almost simultaneously began an initiation of a series of important forward steps in connection with color television studio equipment. His brilliant mind and ability to absorb and digest vast amounts of detailed information soon became evident. Immediately, he found himself the center of consultations, discussions and was besieged as a lecturer to other engineers, as well as laymen, on the subject of color television. His lectures were repeated innumerable times, and finally Mr. Wentworth authored a 450-page textbook entitled *Color Television Engineering*.

While the activities in lecturing and writing are outstanding, they are actually an extracurricular activity in comparison with the serious engineering development work which John has done in his chosen field. His contributions to development of color studio equipment have been extremely broad, including work on colorimetric problems in cameras and receivers. Circuit work in encoders, decoders, switching equipment and distribution equipment were other areas of his activity.

In 1954, only five years after graduation, he was appointed Manager of Television Terminal Equipment Engineering. Most recently Mr. Wentworth was named Staff Engineer in the Broadcast and Television Division, where he has responsibility for the conduct of engineering studies directed toward the development of business opportunities in the field of educational electronics. Mr. Wentworth will also participate in the planning of training programs for customers and prospective customers in the use of Broadcast and Television Division's products.—*J. H. Roe*

LIEBMANN AWARD TO RAJCHMAN

J. A. Rajchman of the RCA Laboratories, Princeton, N. J., was also honored "for contributions to the development of magnetic devices for information processing," by being awarded the 1960 Morris Liebmann Memorial Prize Award by the Institute of Radio Engineers. This is annually awarded to a member of the IRE for a recent important contribution to the radio art.

Mr. Rajchman received his diploma in electrical engineering in 1934 and the degree of Doctor in technical sciences in 1938 from the Swiss Institute of Technology, Zurich, Switzerland. He worked for RCA Manufacturing Co. in 1935 as a student engineer and in 1936 as a research engineer. In 1942 he was transferred to the RCA Laboratories in Princeton where he is presently a member of the research staff, leading research in magnetics and other solid-state computing devices as well as digital systems.

BEST PAPER AWARD TO WILLIAMS

Dr. Roscoe C. Williams, a Member of Technical Staff of the RCA Laboratories, won the 1958 Best Paper Award given by the IRE Professional Group on Ultrasonics Engineering. The paper, entitled "Theory of Magnetostrictive Delay Lines for Pulse and Continuous Wave Transmission," appeared in the PGUE Transactions, Number 7. Dr. Williams joined the technical staff of RCA Laboratories in July 1958 and was formerly with Bell Telephone Labs.

STANDARDS AWARD TO OBERLANDER

At the Eighth Annual Meeting of the Standards Engineers Society, held September 21 and 22 in Boston, a Special Service Citation for Outstanding Service to the Society was presented to **Fred M. Oberlander**, Administrator, Materials Standards, Standardizing, Product Engineering. This was the first such citation awarded by the Society. Mr. Oberlander has held various national offices in SES since its organization in 1948, and was editor of its magazine, *Standards Engineering*, for six years.

EIGHT RCA ENGINEERS RECEIVE IRE FELLOW AWARDS

At a recent Board of Directors meeting, IRE, New York City, it was disclosed that eight RCA engineers had won the highest grade offered by the IRE, that of Fellow. This is bestowed only by invitation on those who have made outstanding contributions to radio engineering or allied fields. Presentation of the awards will be made by the president of the IRE at the annual banquet on March 23, 1960 during the Annual IRE National Convention. Those RCA engineers being honored are as follows:

Recipients

- A. N. Curtiss**, General Manager, West Coast Missile and Surface Radar Div., RCA, Los Angeles, Cal.
- E. O. Johnson**, Manager, High Temperature Products, RCA Semiconductor Div., Somerville, N. J.
- Harwick Johnson**, Research Engineer, RCA Laboratories, Princeton, N. J.
- J. B. Moore**, Staff Engineer, RCA Communications, Inc., New York, N. Y.
- D. S. Rau**, Vice President and Chief Engineer, RCA Communications, Inc., New York, N. Y.
- P. T. Smith**, Technical Director, C. Stellarator Associates, Princeton, N. J.; on leave as Senior Member of Technical Staff, RCA Laboratories, Princeton, N. J.
- A. H. Sommer**, Research Engineer, RCA, Princeton, N. J.
- W. M. Webster, Jr.**, Director, Electronic Research, RCA Laboratories, Princeton, N. J.

Citations

- For contributions to radio and radar technology.
- For contributions to gaseous electronics and semiconductors.
- For contributions to the development of electron devices.
- For improvements in communications coding techniques.
- For contributions to international radio communications systems.
- For contributions to the development of high-power transmitting tubes.
- For contributions in the field of photo-emissive surfaces.
- For contributions to gaseous electronic and solid-state devices.

ENGINEERS IN NEW POSTS

In IEP, **A. S. Kranzley** has been appointed Manager of EDP Product Planning, having previously been Manager of EDP Methods.

Charles J. Hirsch has been appointed Administrative Engineer on the staff of the Vice President, Engineering.

Among personnel assignments within RCA Service Co. are **John J. Lawler**, appointed Manager, Engineering; **Bruce Aaront** named Manager of Field Support Engineering, and **A. L. Christen**, Field Manager.

In Home Instruments Engineering, **L. R. Kirkwood** has been appointed Manager, TV Product Engineering.

In SC&M, appointments are as follows: **L. H. Good**, Manager of Engineering; **R. B. Janes**, Manager, Computer Transistor Engineering; **F. E. Vinal**, Manager, Materials Operation; **D. P. Heacock**, Manager, Entertainment Product Planning; **R. M. Cohen**, Manager, Engineering; **J. M. Spooner**, Plant Manager, Findlay Plant.

TV and Radio "Victrola" Production organization now includes the following managers: **P. A. Collier**, Manufacturing; **J. W. Good**, Manufacturing Engineering; and **T. F. Whitten**, Plant Engineering; **R. W. Sears**, Plant Manufacturing Engineering; **E. G. Young**, Plant Engineering.

The RCA Electron Tube Division announces three new managerships: **L. Gillon**, Marion Plant; **S. M. Hartman**, Equipment Development; and **C. P. Smith**, Engineering.

V. E. Trouant has been appointed Chief Engineer, Engineering Dept. and the following are new managers in the Broadcast and TV Equipment Division: **M. A. Trainer**, Recording Products, High Power and Nucleonics; **J. L. Grever**, Electronic Recording Products; **E. N. Luddy**, High Power Electronics and Nucleonics.

Charles A. Dickinson has been promoted to the position of Manufacturing Manager of the Indianapolis Tube Plant. After coming to the Indianapolis Tube Plant as a Factory Engineer in 1950, he has held the positions of Glass Tube Engineering Manager and Superintendent of Glass Tube Manufacturing. Mr. Dickinson is a graduate of the University of Minnesota, having received both a BS degree in Electrical Engineering and a M.S. degree in Business there.

Robert E. Koehler of the RCA Semiconductor and Materials Division has announced the appointment of **George H. Ritter** as Plant Manager of the new transistor and rectifier manufacturing facility to be constructed in Mountaintop, Pa. and ready for production by mid-1960. His 32-year career with RCA includes many important positions and extensive experience in the manufacture of electronic components.

E. W. Riedweg, who has been Manager of Plant Engineering at the RCA plant at Cambridge, Ohio, has been appointed to the position of General Plant Engineer for the RCA Victor Home Instrument manufacturing operations. With headquarters in Indianapolis, he will have supervision over the construction, maintenance and other plant engineering activities at the Consumer Products plants in Indianapolis, Bloomington and Monticello, Ind., and Cambridge, Ohio.

A. B. Dickinson succeeds K. M. McLaughlin as Plant Manager of the RCA Electron Tube Division Color Kinescope Plant in Lancaster, Pa. A Cornell graduate, Mr. Dickinson joined the RCA Electron Tube Division in 1933 and has since held several key positions with that division.

SINNETT AND PAN IN NEW ASSIGNMENTS

C. M. Sinnett, formerly Mgr., Advanced Development, RCA Victor Home Instruments, was recently named director, Product Engineering Professional Development, by D. F. Schmit, Vice President of Product Engineering. In this capacity Mr. Sinnett will be responsible for administering and co-ordinating Product Engineering Professional Development and Utilization plans and programs in all areas of RCA Engineering operations. Mr. Sinnett is one of the pioneers in the field of management of creative engineering personnel.

Wen Y. Pan was named to the post of Mgr., Advanced Development, RCA Victor Home Instruments, the position formerly held by Mr. Sinnett. Both men have been very active in Advanced Development and Receiver Design for both black and white, and color television circuits. Both have also been active in industry, professional committees, and professional societies work. Dr. Pan has authored numerous technical articles for publication in both outside journals and in the RCA ENGINEER, and RCA Review.

For a complete biography of Mr. Sinnett, see his article (*Ideas*)—"Is There a Limit?" appeared in the RCA ENGINEER, Vol. 1, No. 6. For a biography of Dr. Pan, refer to his article *Development Status of Parametric Amplifiers* (Vol. 4, No. 6.)

CYRIL N. HOYLER

RCA engineers were deeply shocked by the accidental death of Cyril N. Hoyler on October 21 at Moosomin, Saskatchewan. His death followed a collision between a train locomotive and a panel truck in which he and Marvin Phillips, also of the Laboratories staff, were riding. Mr. Hoyler, Manager, Technical Relations, was on an extended lecture trip throughout Northern United States and Canada.

An outstanding lecturer on the subject of electronic science, and a former college professor and research engineer, he had lectured through virtually every state of this country and every province of Canada.

Mr. Hoyler had been with RCA since 1941. He was graduated from Moravian College in 1928 with a B.S. degree and received an M.S. degree in Physics from Lehigh University.

DAVID D. COLE

A great loss was suffered by engineers at RCA when on September 21 David D. Cole passed away after a long illness. Mr. Cole, who had been Chief Engineer of the RCA Victor Television Division at Cherry Hill, N. J., had a distinguished 33-year career in radio and electronic engineering, of which 30 years were with RCA. Mr. Cole graduated from the University of Michigan in 1926 with a B.S. in E.E. degree. Early schooling also included studies in Electrical Engineering at the Michigan College of Mines. In 1928 he completed the GE Test Course and became a design engineer in 1929. In the same year he transferred to RCA at Camden where he also served as design engineer on radio equipment. Mr. Cole subsequently held a number of positions in the RCA Victor Division, and in 1943 became Chief Engineer, Instrument and Standard Parts Engineering, and in 1954 assumed his TV-Division post. Mr. Cole was a member of the IRE and the State Board of Professional Engineers and Land Surveyors.



Dr. C. B. Jolliffe, retiring Vice President and Technical Director, DEP, receives a gift and congratulations from A. L. Malcarney, (center), Executive Vice President and T. W. Massoth, Manager of Administration, DEP.

JOLLIFFE RETIRES

Dr. Charles B. Jolliffe, Vice President and Technical Director, Defense Electronic Products, recently announced his retirement after nearly 25 years of outstanding service with RCA. A member of the Board of Directors of RCA, the National Broadcasting Company, and RCA Communications, Inc., Dr. Jolliffe has also served for nearly six years as Executive Vice President, RCA Laboratories, and for 10 years in numerous important RCA research and engineering positions with RCA.

In the course of a career in which he took part in many of radio's outstanding advances, Dr. Jolliffe participated in international telecommunication conferences in Washington, Copenhagen, Madrid, Paris, Mexico City, Havana, and Cairo, as a representative of the United States while in Government service, and after 1935 as a representative of RCA.

He was born in Manning, West Virginia, on November 13, 1894, the son of Charles E. and Sallie Vandervort Jolliffe. He received his Bachelor of Science degree in 1915 and his Master's degree in 1920 from West Virginia University, and his Ph.D. degree from Cornell University in 1922. He was awarded an honorary LL.D. degree from West Virginia University in 1942.

From 1916 to 1922, except for a period of service in World War I, he taught physics at Ohio State University, West Virginia University, and Cornell University. In 1922, he joined the Radio Section of the Bureau of Standards and served there as a physicist until 1930.

Dr. Jolliffe was appointed Chief Engineer and held that position with the FRC, and its successor, the Federal Communications Commission, for five years. Upon his resignation in November, 1935, he became associated with RCA, and has held the successive positions of Engineer in charge, RCA Frequency Bureau; Chief Engineer, RCA Laboratories; Assistant to the President of RCA; Vice President and Chief Engineer of the former RCA Victor Division, and Executive Vice President in charge of RCA Laboratories Division.

R. F. GUY ASSUMES NEW PREXY POST

Raymond F. Guy, Senior Staff Engineer of NBC, has been elected President of the De Forest Pioneers, a society consisting of former associates of Dr. Lee De Forest, distinguished scientist and inventor. A pioneer in radio, TV and short wave broadcasting, for nearly 30 years he was responsible for planning and construction of all NBC transmitting facilities, including the creation of the Empire State Bldg. TV tower.



ED REPS IN HIGH GEAR FOR THIS ISSUE

The RCA ENGINEER staff takes off its hat to editorial representatives **L. A. Wood**, in the Materials Laboratory at Needham—to **Don Garvin**, in the Tube Division, Lancaster—to **C. A. Meyer**, Tube Division, Harrison—to **Ed Dickey** in the Laboratories at Princeton—and to **R. Samuel** in the semiconductor and materials division, Somerville, for their work in helping to produce this issue.

In the article by **J. J. Sacco, Jr.** dealing with development of square loop ferrite memory cores, there were many photos available which illustrate engineers at work in the Semiconductor Division's new labs at Needham, Mass. Since space did not allow running all of them with Mr. Sacco's article, we are including here those above. Shown from left to right are: **R. Gravel**; **H. Lessoff**, (foreground) and **Y. Nakada** (background); **H. DiLuca**; and **A. Barthe** (left) and **R. Ray** (right).

The RCA ENGINEER has three new Editorial Representatives on its staff. These are **D. Oda**, West Coast Missile and Surface Radar, DEP, Los Angeles, California; **B. J. Goldstone**, Airborne Systems Division, DEP, Camden, N. J.; and **R. J. Mason**, Receiving Tubes, RCA Electron Tube Division, Cincinnati. Their biographies and photos will be included in the next issue.

EXPANDED EDITORIAL ASSISTANCE AT MOORESTOWN

Four RCA engineers have been named to assist **Irmel Brown**, Editorial Representative for the RCA ENGINEER and Associate Editor, Systems and Advanced Systems Planning. This new organization was installed to keep pace with the expanded activities and development at the Moorestown plant, and is as follows:

- I. N. Brown**—Editorial Board Representative and Associate Editor—Systems and Advanced Systems Planning.
- C. Anderson**—Associate Editor, BMEWS
- A. M. Burke**—Associate Editor, Project Management
- H. A. Brelsford**—Associate Editor, Radar Development and Design
- F. Klawnsnik**—Associate Editor, Radar Development and Design

SURFCOM INFORMATION CENTER

The Surface Communications Department of DEP has established an Information Center which embodies the centralization of selected data for purposes of improved communications at minimum cost. The intent of this program is to facilitate business information storage and retrievability for the purposes of obtaining prompt and accurate facts. This area is intended to handle inquiries from all Surface Communications activities regarding day-to-day business transactions. Although specifically developed for Surface Communications, this new business concept can be easily adapted to other RCA locations. Inquiries regarding the details of this program can be directed to Mr. A. S. Hays, Building 1-3, Camden, New Jersey.

—E. O. Selby



Mike Hyduk consults with Miss D. E. Evering, Surfcum Information Center librarian.

RECORD ENGINEERS IN ADVANCED STUDIES

Charles O'D. Knue and **August Skele**, of Record Factory Engineering, and **Herbert W. Hittie**, of Record Development Engineering, are attending Engineering Management Seminars presented by Dr. Shaw, of the Tube Division, at Marion, Indiana.

Purdue University is offering an Off-Campus Graduate Program at North Central High School in Indianapolis with evening classes. Those attending from RCA are: **S. W. Liddle**, **B. J. White**, **A. J. Viere**, **A. G. Evans**, **A. Skele**, **N. L. Covey** and **D. H. O'Herren**.

R. G. Fox has been elected secretary of the Central Indiana Mathematical Society for the 1959-60 term.—*M. L. Whitehurst*

SERVICE CO. REALIGNED

Realignment of operations of Service Company into two major departments—Commercial Service, and Government Service—was announced by D. H. Kunsman, President. The new organization has been effected to keep pace with the tremendous growth of the electronic servicing business which involves all phases of electronics, both industrial and military. Radio and Television Broadcasting, the growing interest in color television, activities in missiles and rockets, industrial electronic inspection and automation equipment, computers, marine, aviation, mobile, and many other types of communications are some of the areas.

FEBRUARY 3-5

Military Electronics, Winter Convention, Biltmore Hotel, Los Angeles.

FEBRUARY 10-12

Solid-State Circuits Conference, AIEE, IRE, Univ. of Penn., Philadelphia.

FEBRUARY 11-13

Electronic Representatives Assoc., Annual Convention, Drake Hotel, Chicago.

FEBRUARY 20-29

Component Parts and Electronic Tubes, International Exhibition, Porte de Versailles, Place Balard, Paris.

MAR. 21-24

Institute of Radio Engineers, National Conv., Coliseum & Waldorf-Astoria Hotel, N.Y.C.

APRIL 4-7

Nuclear Congress, EJC, PGNS of IRE, New York Coliseum, New York City.

APRIL 11-13

Protective Relay Engineers, Annual, A&M College of Texas, College Station, Texas.

APRIL 11-14

Weather Radar Conference, American Meteorological Society and Stanford Research Institute, San Francisco.

APRIL 18-19

Automatic Techniques, Annual Conf., ASME, IRE, AIEE, Cleveland-Sheraton Hotel, Cleveland.

APRIL 19-21

Active Networks & Feedback Systems, International Symposium, Dept. of Defense Research Agencies, IRE, Engineering Societies Bldg., N.Y.C.

G. H. BROWN ACTIVE IN LECTURE CIRCUIT

The schedule of a busy engineer usually includes the presentation of technical information to professional societies and **Dr. George H. Brown**, Vice President, Engineering, is certainly no exception. Listed here are a few of the presentations he has made over the last couple of months. Dinner speech *The History of Some Antennas*, Symposium on Antennas and Wave Propagation, sponsored by the Cedar Rapids, Iowa, Section of the IRE; *Organizing the Engineering Program*, Special Conference of the American Management Association, New York; *Research—The Dynamic Ingredient of Standardization*, National Conference on Standards, American Standards Association, Detroit, Michigan; *The Development of Color Television in the United States*, Benelux Section of the IRE, The Hague, Holland; *The Development of Color Television in the United States*, International Telecommunications Union, Geneva, Switzerland.

FOUR SEPARATE SC&M DEPARTMENTS

A new organization structure, designed to meet current and future sales and operational requirements of the RCA Semiconductor and Materials Division, was announced by **Dr. A. M. Glover**, Vice President and General Manager of the Division. The new organization includes four product departments with managers named as follows: **N. H. Green**, Manager of Entertainment Semiconductor Products; **K. M. McLaughlin**, Manager of Computer Products and Materials Department; and **B. V. Dale**, Manager of the Micromodule Department. A manager of the Division's Industrial Semiconductor Products Department will be announced later.

NEW IEP PLANT

A new plant for the manufacture of RCA industrial electronic products will be constructed in the Washington-Canonsburg, Pa., area. The plant, the second new Pennsylvania facility to be announced by RCA recently will provide urgently needed space to accommodate RCA's expanding industrial electronic product activity.

RCA ENGINEER EDITORIAL REPRESENTATIVES

DEFENSE ELECTRONIC PRODUCTS

F. D. WHITMORE, *Chairman, Editorial Board*

Editorial Representatives

- JOHN BIEWENER, *Airborne Systems Division
Camden, N. J.*
- I. N. BROWN, *Missile and Surface Radar
Engineering, Moorestown, N. J.*
- R. D. CRAWFORD, *Design Development Engineering,
Airborne Systems Division, Camden, N. J.*
- R. W. JEVON, *Missile Electronics and Controls,
Burlington, Mass.*
- B. J. GOLDSTONE, *Systems Engineering,
Airborne Systems Division, Camden, N. J.*
- D. ODA, *West Coast Engineering,
Los Angeles, Calif.*
- E. O. SELBY, *Surface Communications
Engineering, Camden, N. J.*
- F. W. WHITTIER, *Development Engineering,
Camden, N. J.*
- H. L. WUERFFEL, *Central Engineering,
Camden, N. J.*

INDUSTRIAL ELECTRONIC PRODUCTS

C. W. SALL, *Chairman, Editorial Board*

Editorial Representatives

- N. C. COLBY, *Communications Engineering,
Camden, N. J.*
- C. E. HITTLE, *Hollywood Engineering,
Hollywood, Calif.*
- C. D. KENTNER, *Broadcast Transmitter and Antenna
Engineering, Camden, N. J.*
- T. T. PATTERSON, *Electronic Data Processing
Engineering, Camden, N. J.*
- D. S. RAU, *RCA Communications, Inc.
New York, N. Y.*
- J. H. ROE, *Broadcast Studio Engineering,
Camden, N. J.*
- J. E. VOLKMANN, *Industrial and Audio Products
Engineering, Camden, N. J.*

ASTRO-ELECTRONIC PRODUCTS DIVISION

Editorial Representative

L. A. THOMAS, *Engineering, Princeton, N. J.*

RCA LABORATORIES

Editorial Representative

E. T. DICKEY, *Research, Princeton, N. J.*

RCA VICTOR RECORD DIVISION

Editorial Representative

M. L. WHITEHURST, *Record Engineering
Indianapolis, Ind.*

The Editorial Representative in your group is the one you should contact in scheduling technical papers and arranging for the announcement of your professional activities. He will be glad to tell you how you can participate.

RCA ELECTRON TUBE AND SEMICONDUCTOR & MATERIALS DIVISIONS

J. F. HIRLINGER, *Chairman, Editorial Board*

Editorial Representatives, RCA Electron Tube Division

- W. G. FAHNESTOCK, *Conversion Tube Operations,
Lancaster, Pa.*
- J. DEGRAAD, *Black & White Kinescopes,
Marion, Ind.*
- D. G. GARVIN, *Entertainment Tube Products,
Lancaster, Pa.*
- R. J. MASON, *Receiving Tubes, Cincinnati, Ohio*
- T. M. CUNNINGHAM, *Entertainment Tube Products,
Harrison, N. J.*
- J. KOFF, *Receiving Tubes, Woodbridge, N. J.*
- H. S. LOVATT, *Power Tube Operations,
Lancaster, Pa.*
- F. H. RICKS, *Receiving Tubes, Indianapolis, Ind.*
- H. J. WOLKSTEIN, *Industrial Tube Products
Harrison, N. J.*

Editorial Representatives, RCA Semiconductor & Materials Division

- L. A. WOOD, *Needham Materials Lab,
Needham, Mass.*
- RHYS SAMUEL, *Micromodules, Somerville, N. J.*
- HOBART TIPTON, *Semiconductor Devices,
Somerville, N. J.*
- J. D. YOUNG, *Findlay, Ohio*

RCA VICTOR HOME INSTRUMENTS

K. A. CHITTICK, *Chairman, "Cherry Hill" Editorial Board*

Editorial Representatives

- D. J. CARLSON, *Advanced Development
Engineering, Cherry Hill, N. J.*
- E. J. EVANS, *Resident Engineering,
Bloomington, Ind.*
- F. T. KAY, *TV Product Engineering,
Cherry Hill, N. J.*
- J. OSMAN, *Resident Engineering, Indianapolis, Ind.*
- W. S. SKIDMORE, *Radio "Victrola" Product
Engineering*

RCA SERVICE COMPANY

Editorial Representatives

- W. H. BOHLKE, *Consumer Products Service
Department, Cherry Hill, N. J.*
- M. W. TILDEN, *Government Service Department,
Cherry Hill, N. J.*
- E. STANKO, *Technical Products Service Department,
Cherry Hill, N. J.*



RCA ENGINEER

A TECHNICAL JOURNAL PUBLISHED
BY PRODUCT ENGINEERING.
"BY AND FOR THE RCA ENGINEER"

RADIO CORPORATION OF AMERICA