APPENDIX

Innovation Histories

INTRODUCTION

In the course of collecting and cross-checking the data on the functional locus of innovation coded in chapters 2 and 3 of this book, my students and I generated what were, in effect, minihistories of the innovations under study. I present these as a data base for others interested in exploring the functional source of innovation. Also, I will mention here a few hard-won bits of practical wisdom regarding data collection on this topic that others may find useful.

Suggestions Regarding Data Collection

Our data collection strategy was built around the principle of *independent* access to the various functional categories of firms and individuals that may have played a role in an innovation under study. That is, we searched all likely functional communities directly for evidence of possible involvement in the innovation process. This strategy proved very useful. Since "success has many fathers," reliance on a single data source as a gateway to others would almost certainly have introduced a systematic bias to our data. For example, a data collection strategy that relied on manufacturers to point out the innovation-related contributions of users and others would predictably produce findings biased toward the contributions of manufacturers.

A short anecdote may serve to give the reader the flavor of the problem. We inquired of the first responsible project engineer at what was apparently the first commercial manufacturer of an instrument as to its innovation history. "All mine," he said. When we ran a computer search of the chemical literature, we found three articles, published several years earlier, describing experimental versions of the innovation and the interesting results obtained through their use. A parallel search of trade journal ads produced information about a functionally equivalent Canadian instrument that had apparently been introduced to the marketplace prior to the introduction of the U.S. company's version.

We went back to our original informant to discuss these findings. He admitted, in honest confusion, that he was aware of the articles and product we had found, but he had not mentioned them to us because he did not consider them to be related to his innovation. To be sure, the function and operating principles of the experimental devices and the Canadian instrument were the same, but the *product engineering* of his device was entirely his own—and this had been the innovation, in his view.

Our data collection procedure used three major elements for each sampled innovation involved. First, we started our work by identifying the first firm to develop and commercialize an innovation and the date of commercial introduction. This was done by asking personnel of firms now manufacturing "me-too" devices if they knew which was the first firm to commercialize them *and* by asking expert users, manufacturers, and suppliers of the innovation. Ambiguities were cleared up by searching the technical or trade literature and seeking the earliest references to, advertisements regarding, and/or new product announcements for the innovation in question.

When the first commercializing firm and the date of commercialization were firmly established, we interviewed, either in person or by telephone, everyone at the commercializing firm who claimed substantial, firsthand knowledge of the innovation work. As a routine part of a structured interview, each interviewee was asked to provide the names of others he or she felt might have some important information to contribute, and these individuals were contacted in turn.

Second, in addition to our interviews with personnel in the first commercializing firms, we searched the technical and trade literature of the period *prior* to the first commercial innovation, seeking references to products or processes functionally similar to the innovation being studied. Authors of relevant articles were contacted and interviewed, usually by telephone. As part of the interview, they were asked for the names of knowledgeable people in user and other firms, and these people were subsequently contacted.

Where we could identify very early purchasers of the commercialized innovation, we also canvassed these firms for information regarding their contribution, if any, to the innovation and/or the name of individuals who might have information bearing on the innovation process, and so forth. Thus, insofar as possible, we interviewed all key individuals identified as being directly involved with each innovation studied.

Third, information from the various sources was assembled, discrepancies were noted, and interviewees with information bearing on the discrepancies were contacted again for further discussion. Some areas of confusion were cleared up by means of this process; others were not. We always attempted to accurately preserve differing versions of events where they existed and did not attempt to determine "who was right." If proper coding of an item would require us to make such a judgment, we coded it NA (not available).

Other Matters

Our ability to accurately collect data regarding innovations that had often been developed a number of years ago was greatly enhanced by our definition of an innovator (discussed earlier) as one who had developed an innovative product or process to a concrete, usable state. Development work carried to this stage usually leaves many contemporaneously generated documents and artifacts—reports, publications, prototypes—that are most helpful in reconstructing innovation process events.

Defining the innovator as the first to develop a product or process to a useful state ignores any contributions by firms or individuals that might be valuable but that do not reach the state of implementation. This is a loss, but I am not sure how much of a loss. As has been shown by studies such as Project Hindsight,[1] any innovation is built upon a great web of earlier developments in technology and science stretching back, certainly, to the Renaissance and even earlier. Is it meaningful to try and allocate the locus of a particular innovation among all these precursors? For our purposes I think not. We are interested in determining who builds upon prior art and science to produce very specific innovations. In practice I find that at this level of specificity the people who innovate have a particular need or market in mind that can only be served by a completed device. Since there is little benefit to be derived from half an innovation, I find, as a practical matter, that innovators strive to bring the innovations they work on to a useful state. Therefore, my definition of *the* innovator as the firm or individual that first develops a specific product or process to a completed, useful state appears to accurately reflect the realities of this type of innovation.

Finally, in this book I focus on the three innovation categories of user, supplier, and manufacturer. For other research purposes, one might wish to segment such major categories more finely. For example, one could divide the general category of users of scientific instruments into subsets such as research users, teachers, and pupils—each of which use a scientific instrument in different ways. Such subsets will cause no trouble in analyses of the functional locus of innovation as long as they are made clear. For example, if the distinction between research/user of scientific instruments and teacher/user is understood, one can separately analyze the innovation-related benefits attendant upon firms holding each of these types of functional relationship and determine the appropriate role of each in the innovation process. (Appropriate segmentation of user subsets can sometimes be aided by application of segmentation techniques often used by marketing researchers.[2])

Notes

1. Raymond S. Isenson, "Project Hindsight: An Empirical Study of the Sources of Ideas Utilized in Operational Weapon Systems," in *Factors in the Transfer of Technology,* ed. William H. Gruber and Donald G. Marquis (Cambridge, Mass.: MIT Press, 1969), 155–76.
2. Glen L. Urban and John R. Hauser, *Design and Marketing of New Products* (Englewood Cliffs, N.J.: Prentice-Hall, 1980).

DATA SET FOR SCIENTIFIC INSTRUMENT INNOVATIONS

The data set for scientific instrument innovations contains information on the gas chromatograph (GC), the nuclear magnetic resonance (NMR) spectrometer, and the transmission electron microscope (TEM). In the following pages the innovation history of each basic instrument type is followed by histories of the major improvements to it that have been commercialized over the years. The histories of all the innovations not coded NA in chapter 2 will be found in this data set, with two exceptions: the innovations identified in our study of ultraviolet absorption spectrophotometry and all minor improvements to electron microscopy. In these instances we have no data beyond that presented in chapter 2.

Selection criteria for the samples in this data set will be found in chapter 2.

THE GAS CHROMATOGRAPH (GC)

The gas chromatograph is used for the quantitative and qualitative analysis of unknown chemical mixtures. It provides much faster and more accurate analyses than earlier wet chemistry methods and is very frequently used.[1] The GC operates by physically separating a chemical mixture into its components. The mixture is passed in the form of a gas over a surface containing a partitioning agent that selectively *ad*sorbs its components, thus slowing the rate of movement of some components relative to others. The adsorbing surface is contained in a column. Gas injected into one end of the column as a mixture (combined with carrier gas) emerges from the other end as a sequence of components that pass in series through any of several types of detectors for identification.

Development History

The analytical technique embodied in the gas chromatograph—gas–liquid partition chromatography—can be traced back to a 1941 paper by A.J.P. Martin and R.L.M. Synge.[2] This paper suggested the idea and described the process theoretically—an accomplishment for which the authors were later awarded a Nobel Prize. In 1952 Martin suggested to A. T. James—a young scientist working with him at the Mill Hill Medical Research Laboratories in England—that he try to build a GC along the lines outlined in the 1941 paper. James did, and the device worked. Their initial paper in 1952 described the apparatus and gave some results they had obtained with it.[3]

After the publication of the James and Martin article, many scientists in industry and universities began to experiment with the technique. By 1953–54 there were perhaps two dozen homemade GC devices in use around the world.[4]

Commercialization

Commercial GCs were first produced in 1954–55. British instrument firms (among them Griffin and George, London, and Metropolitan Vickers Electrical Company, Manchester) began producing commercial instruments before American firms entered the market. The first two American firms to begin commercial production in the spring of 1955 were the Burrell Corporation and the Perkin–Elmer Corporation.[5] In the instance of Perkin–Elmer, we have learned by interview that the transfer to commercialization came about as follows: Dr. Z. V. Williams, vice president of Perkin–Elmer, often traveled to England on company business and had contact among scientists there (among other products, Perkin–Elmer sold spectrophotometers to industrial and university scientists). On one of these trips in 1953, Williams heard of gas–liquid partition chromatography and suggested to Harry Hausdorff, a young employee of Perkin–Elmer with a background in chemistry, that it might be worth looking into as a commercial possibility. Hausdorff made a trip to England, visited laboratories where homebuilt gas chromatography apparatus was in use, attended a lecture at Oxford on gas chromatography, and came back (he recalls) with about 20 journal articles on the subject. Dr. Hausdorff was convinced of the commercial potential of gas chromatography after his trip but had some difficulty interesting his superiors in the project (they noted that the device had no optical parts and optics was, after all, Perkin–Elmer's forte). Eventually, Hausdorff prevailed and was allowed to proceed with commercialization.[6]

Notes

1. National Research Council of the National Academy of Sciences, *Chemistry: Opportunities and Needs* (Washington, D.C.: National Academy of Sciences, 1965).
2. A.J.P. Martin and R.L.M. Synge, "A New Form of Chromatogram Employing Two Liquid Phases ," *Biochemical Journal* 35 (1941): 1358–68.
3. A. T. James. and A.J.P. Martin, "Gas–liquid Partition Chromatography: The

Separation and Micro-estimation of Volatile Fatty Acids from Formic Acid to Dodecanoic Acid," *Biochemical Journal* 50 (1952): 679–90.

4. L. J. Ettre, personal communication while at Perkin–Elmer Corp., Norwalk, Conn.

5. L. J. Ettre, "The Development of Gas Chromatography," *Journal of Chromatography* 112 (1975): 1–26.

6. Dr. H. H. Hausdorff, interview at Perkin–Elmer Corp., Norwalk, Conn., 1971.

Temperature Programming

Raising the temperature of the gas chromatograph allows one to analyze substances that volatilize at greater-than-room temperatures. Raising the temperature of the instrument during an analysis in a preprogrammed manner allows one to rapidly analyze a sample containing components of very different boiling points. This very useful improvement in performance was obtained by modifying the various components of the GC to tolerate high temperatures and then installing the entire instrument in a special-purpose temperature-controlled oven.

Development History

Courtney Phillips appears to have originated temperature programming at Oxford University in 1952.[1] Gas chromatographs with temperature programming were then built by numerous users for their own use. Over 20 publications related to temperature programming appeared in the literature prior to the appearance of the first commercial instrument on the marketplace.[2]

Commercialization

Frank Martinez was a glass blower at Du Pont who was involved in constructing several of the temperature-programmed GCs built at Du Pont for the use of that firm's scientists. When interest was shown in the device by non–Du Pont people, Martinez left the firm and formed F&M Scientific Corporation in April 1959 to manufacture a Du Pont-designed instrument that included temperature programming—reportedly a design developed by S. Dal Nogare, a Du Pont scientist. This new firm was the first to offer temperature-controlled GCs for commercial sale.

Notes

1. J. Griffiths, D. James, and C. Phillips, "Gas Chromatography," *Analyst* 77 (December 1952): 897–904.

2. W. E. Harris and H. W. Habgood, "Annotated Bibliography of Programmed Temperature Gas Chromatography: 1952–1964, Part I. 1952–1961," *Journal of Gas Chromatography* 4 (April 1966): 144–46.

Capillary Column

The capillary column is a long thin tube coated on the inside with partitioning agent. When the short, granule-packed column normally used in a GC is replaced by such a column, the sensitivity and resolution of the instrument is significantly improved.

To understand the reason for this improvement I must elaborate slightly on my previous description of the operating principles of a GC. As noted earlier, GCs separate the components of a gaseous chemical mixture by passing them through a granule-packed column. A coating on the granules adsorbs (clings to) some components of the mixture more strongly than others. The more strongly a particular component is adsorbed, the more slowly it is moved through the column by the stream of carrier gas passing steadily through the column. The result of this effect is the physical separation of the components of the mixture, with those least strongly adsorbed emerging from the end of the column first.

Efficiency of component separation attainable by the GC is clearly lessened because the gas must pass through a column of granules: Gas flow will inevitably be less rapid between some granules than others, and some paths available to gas molecules through the maze of granules will be longer than others. The capillary column, being a simple hollow cylinder coated with partitioning agent, greatly reduces these sources of error.

Development History

The capillary column concept was developed by Marcel Golay, a mathematician who worked as a consultant to Perkin–Elmer Corporation. According to Harry Hausdorff,[1] the gas chromatography group at Perkin–Elmer set Golay the task of developing a "universal" column. Their motivation was to reduce the number of types of specialized prepared granular columns they had to keep in inventory to service customer needs. Golay presented the concept of the capillary column in 1957.[2] In 1958 both he[3] and a user group[4] presented practical results obtained with such columns at a conference in Amsterdam.

Commercialization

Perkin–Elmer, the employer of Golay, observed the strong user interest displayed in capillary columns and quickly commercialized them, first making them available in March 1959.

Because Perkin–Elmer was the first to develop the capillary column as well as the first to commercialize it, the firm was in a position to patent the innovation and did so. Interestingly, however, tentative moves to enforce the patent were abandoned in the face of user protests. According to Perkin–Elmer interviewees, scientist/users working at nonprofit institutions felt that free sharing of innovations was the established norm in the field.

Notes

1. Dr. H. H. Hausdorff, conversation with the author at Perkin–Elmer Corp., Norwalk, Conn., 1975.
2. M. Golay, in *Gas Chromatography 1957: Lansing Symposium,* ed. V. Coates, H. Noebels, and I. Fogerson (New York: Academic Press, 1958), 1–13.
3. M. Golay, in *Gas Chromatography 1958: Amsterdam Symposium,* ed. D. Desty (London: Butterworths, 1958), 36–55.
4. G. Dijkstra and J. de Gory, in D. Destry, ed., *Gas Chromatography 1958,* 36–55.

Silanization of Column Support Material

As mentioned earlier, gas chromatography is a physical means of separating chemical mixtures. Since any chemical reactions that occur within the instrument itself will cause false results, it is important that materials that come into contact with the sample be chemically inert with respect to it. A major step forward in rendering the granular column packing material (column support material) inert to important classes of sample material was a chemical treatment called silanization. Prior to the introduction of a quality-controlled silanized support material, investigators had great difficulty analyzing such materials as steroids, alkaloids, bile acids, and pesticides with the GC: These had tended to break down owing to chemical interaction with earlier support materials.

Development History

Silanization of column support material was developed by E. C. Horning, M. Horning, W. Van den Heuvel, and others, at the National Institutes of Health (NIH), Bethesda, Maryland, and at Baylor University College of Medicine, Houston, Texas. The work was performed in the 1958–64 period and resulted in numerous publications.

Commercialization

In the late 1950s and 1960s, E. C. Horning and his colleagues were involved with work on atherosclerosis at NIH. For their work they required special chemicals that were available from only two companies. One of these, Applied Science Libraries, State College, Pennsylvania, was a company founded by a former chemistry professor, Dr. Arthur Rose, of Pennsylvania State University. Horning became a customer of Applied Science Laboratories and a friendship developed between Horning and Rose. When Horning developed his novel column support material, he convinced the firm to enter the business of producing column supports.[1]

The problems involved in producing large batches of Horning's silanized column support material of consistent quality were addressed and solved by Applied Science Laboratories personnel. Gas-Chrome Q, the first commercially produced silanized column support material, was introduced to the market by Applied Science Laboratories in December 1964. The first competitors, F&M Scientific and Johns Manville, entered the market approximately one and a half years later.

Note

1. Dr. E. C. Horning, Baylor University College of Medicine, Houston, Tex., and R. Kruppa, Applied Science Laboratories, State College, Penn., telephone interviews, 1975.

Thermal Conductivity (TC) Detectors

When components of a chemical mixture being analyzed emerge from the partitioning column of a gas chromatograph, their presence must be detected. The first commercialized means of performing this task was the thermal conductivity detector. "Basically, a TC cell consists of a block (usually metallic) containing a cavity through which the carrier gas flows. A heated element (thermistor or resistance wire) is positioned in the cavity and loses heat to the block at a rate depending upon the TC of the gas. Since absolute measurement of TC is difficult, a differential means is usually employed. Thus, for example, two cavities can be drilled in the block, each one containing an element. Only carrier gas passes through one cavity and the column effluent passes through the other."[1] The difference in thermal conductivity is then measured in terms of the difference in electrical resistance of the two detectors.

Development History

The use of thermal conductivity for detection of gases is itself an old concept. It was apparently first applied to gas chromatography in 1954 by N. H. Ray, a scientist at ICI in England.[2] Ray visited the A.J.P. Martin and A. T. James laboratory (according to Martin, the originator of gas chromatography) and expressed an interest in examining compounds that were not detectable by titration. Martin suggested that Ray try a TC detector as this technique had already been used successfully by Caesson at Shell Amsterdam as a detector for his gas-solid chromatograms.[3]

Commercialization
Knowledge of thermal conductivity detection was widespread and detectors embodying this principle were installed on all of the early commercial gas chromatographs introduced around 1954 by firms such as Griffin and George, London, and Perkin-Elmer, Norwalk, Connecticut.

Notes

1. Alexander E. Lawson, Jr., and James M. Miller, "Thermal Conductivity Detectors in Gas Chromatography," *Journal of Gas Chromatography* 4 (August 1966): 273–84.
2. N. H. Ray, "Gas Chromatography: II. The Separation and Analysis of Gas Mixtures by Chromatographic Methods," *Journal of Applied Chemistry* 4 (February 1954): 82–85.
3. A. Martin, "The Past, Present and Future of Gas Chromatography," in *Gas Chromatography 1957: Lansing Symposium,* ed. V. Coates, H. Noebels, and I. Fogerson (New York: Academic Press, 1958), 237–47.

Argon Ionization Detector

The argon ionization detector is a great deal more sensitive to the presence of organic compounds than earlier detectors. Its operation is based on the observation by J. E. Lovelock that argon when used as a carrier gas could be ionized and then would transfer significant amounts of excitation energy to any organic vapors that were present. A beta ray ionization detector could then be used to sensitively detect any such transfer as a loss in ionization current. This in turn would signal the presence of the vapor.[1]

Development History
Lovelock, an English scientist without organizational affiliation, had been working with fatty acids in red blood cells and had difficulty in achieving good results with existing detectors used in gas chromatography. He turned his attention to this problem and developed the argon ionization detector around 1957.[2] Lovelock patented the innovation.

Commercialization
The argon ionization detector was first commercialized in 1959 by W. G. Pye and Company, an English manufacturer of gas chromatographs. Pye had begun production of GCs early on, 1954–55. Many of their customers, the petrochemical companies, had complained about problems with existing detectors (e.g., gas density balance and thermoconductivity). Pye knew of Lovelock's work with the new argon ionization detector, sought him out, and licensed his detector. Shortly after Pye's commercial introduction, other instrument makers began producing this detector by license from Lovelock.[2]

Notes

1. J. E. Lovelock, "A Sensitive Detector for Gas Chromatography," *Journal of Chromatography* 1 (1958): 35–46.

2. Dr. S. R. Lipsky, Yale Medical School, New Haven, Conn., telephone interview, 1975. (Lovelock and Lipsky collaborated in 1958–59 to develop the electron capture detector. Based on his acquaintanceship with Lovelock, Lipsky felt able to comment on the history of the argon ionization detector.)

Electron Capture Detector

The electron capture detector is an improved version of the argon ionization detector (see preceding entry). It has great sensitivity to materials such as pesticides, which are often present in samples in trace amounts only.

Development History

Lovelock and Lipsky met at a meeting of the New York Academy of Sciences in 1958–59 and decided to combine their efforts in order to improve GC detectors. Lovelock went to New Haven for six months as Lipsky was affiliated with the Yale Medical School. Together, they developed the electron capture detector.[1]

Commercialization

The electron capture detector was first commercialized by Barber-Coleman in 1960. Information on the device was transferred to Barber-Coleman by Lipsky who consulted for that firm. Shortly after the Barber-Coleman introduction, many firms began producing electron capture detectors.

Lipsky reports that his relationship with Barber-Coleman developed as a result of that firm being a supplier of GCs to his laboratory.[2]

Notes

1. J. E. Lovelock and S. R. Lipsky, "Electron Affinity Spectroscopy—A New Method for the Identification of Functional Groups in Chemical Compounds Separated by Gas Chromatography," *American Chemical Society Journal* 82, no. 1 (20 January 1960): 431–33.

2. Dr. S. R. Lipsky, Yale Medical School, New Haven, Conn., telephone interview, 1975.

Flame Ionization Detector

The flame ionization detector was introduced at approximately the same time as the argon ionization detector (see above) and provided similar major advantages over previously existing detectors used in gas chromatography. The detector measures the effect of organic vapors on the electrical conductivity of a flame.

Development History

The flame ionization detector was developed independently and nearly simultaneously by two groups: I. G. McWilliam and R. A. Dewar of ICI[1]; and J. Harley of the Engineering Research Section, South African Iron and Steel Industrial Corporation, with M. Nel and V. Pretorius of the University of Pretoria, South Africa.[2] There is some controversy over which group had priority. Patent rights, however, were obtained by ICI and licenses were issued by that firm to instrument manufacturers.

Commercialization

The flame ionization detector was described at an international symposium on gas chromatography in 1958[3] and also in an article in *Nature* in 1958.[4] Instrument firms immediately saw the commercial value of the idea and proceeded with commercialization even before the ICI patent was issued. The first firm to put the detector in the marketplace was apparently Perkin–Elmer Corporation in September 1959.

Notes

1. I. G. McWilliam and R. A. Dewar, "Flame Ionization Detector for Gas Chromatography," *Nature* 181, no. 4611 (15 March 1958): 760.
2. J. Harley, W. Nel, and V. Pretorius, "Flame Ionization Detector for Gas Chromatography," *Nature* 181, no. 4603 (18 January 1958): 177–78.
3. I. McWilliam and R. Dewar, in *Gas Chromatography 1958: Amsterdam Symposium,* ed. D. Desty (London: Butterworths, 1958), 142–45.
4. McWilliam and Dewar, "Flame Ionization Detector," 760.

Mass Spectrograph Detector

The mass spectrograph is an instrument that distinguishes molecules on the basis of their mass. It is an important instrument and widely utilized in its own right. Applying it as a detector to the gas chromatograph was a logical step but difficult to achieve—the gaseous output of a gas chromatograph is normally too large and too rapidly changing for a mass spectrograph to utilize. Several successful means (e.g., a device that separates the high volume of carrier gas from the sample gas) have been used to adapt the output of the gas chromatograph to the input requirements of the mass spectrograph.

Development History

The first successful linkage of a mass spectrograph and a gas chromatograph appears to be that of R. S. Gohlke, a researcher at Dow Chemical.[1] In 1957 Gohlke used a Bendix time of flight mass spectrograph owned by Dow as his detector. In 1960, L. P. Lindeman and J. L. Annis published a means to link the gas chromatograph to a magnetic mass spectrograph.[2] In the early 1960s Ryhage also developed and patented a jet separator linkage for this purpose.[3]

Commercialization

When Gohlke published his paper on the linkage he had accomplished between the gas chromatograph and the Bendix time of flight mass spectrograph, Bendix personnel heard about the achievement and produced a commercial version in January 1959. Their system was, however, expensive and difficult to operate and was not a commercial success. In the early 1960s Ryhage attempted to commercialize his linking device on his own and failed. A Swedish company, LKB, then obtained exclusive rights to the Ryhage patent and successfully commercialized the device in November 1965.

Notes

1. R. Gohlke, *American Chemical Society, Division of Petroleum Chemistry Preprints* 2, no. 4, D77–D83 (1957).
2. L. P. Lindeman and J. L. Annis, "Use of a Conventional Mass Spectrometer as a Detector for Gas Chromatography," *Analytical Chemistry* 32, no. 13 (December 1960): 1742–49.
3. Klaus Biemann, Professor of Chemistry, MIT, conversation at MIT, Cambridge, Mass., 1975. Professor Biemann developed a GC/MS linking device that has been

commercialized by both Consolodated Electrodynamics and Varian Associates, and he is intimately familiar with related work in this field.

Gas Sampling Valve with Loop

The gas sampling valve with loop is a simple innovation that had the effect of making the gas chromatograph into an instrument that could conveniently yield quantitative as well as qualitative results. To achieve this end it is necessary to inject a precisely known volume of the sample. The means chosen was the addition of a prechamber to the input valve of the gas chromatograph in the form of a loop of metal tubing. A gas sample of known volume and pressure was accumulated in this prechamber prior to injection into the gas chromatograph itself.

Development History

Investigators interested in achieving quantitative results with a gas chromatograph utilized various ad hoc means to this end. To my knowledge, however, no one made an addition to the instrument to accomplish that end conveniently and routinely prior to H. H. Hausdorff, E. Watson, and Bresky of Perkin–Elmer Corporation; they developed the gas sampling valve with loop at Perkin–Elmer[1] and assigned it to that firm. E. Watson received a patent for the innovation.[2]

Commercialization

Perkin–Elmer's gas chromatography group was motivated to develop the gas sampling valve with loop by the commercial possibilities associated with making the GC a more convenient instrument to use in quantitative studies. The same commercial assessment led them to quickly commercialize the valve, first making it available in 1956.

Notes

1. H. H. Hausdorff and L. J. Ettre, interview at Perkin–Elmer Corp., Norwalk, Conn., 1975.
2. U.S. Patent No. 2,757,541.

Process Control Chromatography

Gas chromatographs are extensively used in the on-line control of chemical process plants. Adopting the GC to this purpose required the development of special valves that would automatically sample a stream of gases moving through a plant. It also required the improvement of the long-term stability of GC performance: Users needed to be sure that a change in readings indicated a real change in plant performance rather than merely variations in performance of the monitoring instrumentation.

Developmental History

Early work in adapting GCs to process control was carried out by users in chemical and petroleum firms. An early U.S. application of a GC to this end was by researchers at Esso, who in 1956 reported on an application in an Esso refinery in Linden, New Jersey.[1] Another early developer was Keulemans, a researcher at Shell in the Netherlands.

Commercialization

Three companies were active in the introduction of process control gas chromatography: Beckman Instruments, Consolidated Electrodynamics, and Podbielniak Corporation. There is some uncertainty as to which of these firms was first on the market—probably Podbielniak was first. Seaton Preston, then at Podbielniak, reports that firm's first sale of a process control gas chromatograph to an Italian customer in 1956. The other two firms did not enter the market until 1957.[2] Podbielniak's equipment adopted the sampling valve developed by Keulemans of Shell. Initially, they built the valve in-house. Later, they turned to the Dutch firm that had fabricated valves for Keulemans.[3]

Notes

1. "Gas Chromatography Growing," *Chemical and Engineering News* 34, no. 15 (9 April 1956): 1692–96.
2. "Chromatography Reaches the Plant," *Chemical and Engineering News* 35, no. 33 (19 August 1957): 77–79.
3. Seaton Preston, telephone interviews, 1975. (Preston was an employee of Podbielniak Corp. at the time of the commercialization of process control gas chromatography.)

Preparative Gas Chromatography

Gas chromatographs used to identify chemicals in a mixture were only large enough to isolate a sufficient amount of each chemical to allow identification: They were not large enough to isolate sufficient material that would be useful in further chemical procedures. Since the material isolated by gas chromatography was very pure, it seemed desirable to scale up the process to the point at which useful amounts of chemical could be isolated through gas chromatographic techniques. Scaling up was achieved by increasing column size, by installing multiple columns, and by employing other means.

Development History

D.E.M. Evans and J. C. Tatlow at Birmingham University in England reported scaling up a GC column to separate fluorinated hydrocarbons in 1955.[1] Others soon reported other scale-up techniques to achieve preparative gas chromatography.[2]

Commercialization

The first firm to commercialize a preparative GC was Beckman Instruments Corporation, which introduced its Megachrom in March 1958. This device utilized larger-than-standard multicolumns that operated in parallel. A recycling system for the carrier gas (helium) was used for cost efficiency. D. Carle, one of the developers of the Megachrom at Beckman, advises that this scale-up approach was not copied from a user instrument but was original to Beckman.[3]

Notes

1. D.E.M. Evans and J. C. Tatlow, "The Reactions of Highly Fluorinated Organic Compounds. Part VIII. The Gas-chromatographic Separation on a Preparative Scale, and Some Reactions, of 3*H*- and 4*H*-Nonafluoro*cyclo*hexene," *Journal of the Chemical Society* (London) 1955: 1184–88.
2. D. Ambrose and R. R. Collerson, "Use of Gas-Liquid Partition Chromatography as a Preparative Method," *Nature* 177, no. 4498 (14 January 1956): 84.
3. D. Carle, Beckman Instruments Corp., telephone interview, 1975.

THE NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROMETER

The nuclear magnetic resonance spectrometer identifies structural properties of molecules. It operates by simultaneously applying a steady magnetic field and a radio frequency signal to a sample of atoms or molecules. Adjustment of the frequency of the radiation and the strength of the magnetic field produces variations in the amount of radiation absorbed. The absorption is the result of NMR and occurs in spectra that are characteristic for different molecules and atoms and that can be used to identify them.

Development History

The original discovery of the NMR phenomenon was made by Felix Bloch, Professor of Physics at Stanford University, in 1946.[1] Bloch and E. M. Purcell, Professor of Physics at Harvard University, received a Nobel Prize for their research related to the phenomenon. The usefulness of the innovation to chemists was created with a discovery of the so-called chemical shift—the shift of nuclear magnetic resonant frequencies that occurs as a result of interactions with nearby atoms in a sample. This provides information about the chemical structure of organic molecules and other materials. The chemical shift phenomenon was discovered by W. G. Proctor and F. C. Yu in 1950.[2] The authors worked for Bloch at Stanford University. W. C. Dickinson[3] also played an important role in this discovery. The technique was further developed by H. S. Gutowsky.[4]

Commercialization

Prior to commercialization, there were only two NMR spectrometers in existence, those of Bloch at Stanford and Purcell at Harvard. Russell Varian, who had studied physics at Harvard, convinced Bloch to patent NMR, which Bloch did—receiving a very broad patent. Russell and his brother then took a license to the NMR patent, which they transferred to Varian Associates when they founded the company in April 1948. The first commercial NMR spectrometer was built by Varian Associates in 1950–51. The first three high-resolution NMR spectrometers commercialized were delivered to Humble Oil, Shell Development Corporation, and the Du Pont experimental station. These were operating by 1952.

The circuits used in Varian's first spectrometer had been published in the literature. As time went on, however, researchers employed by Varian Associates made significant contributions to the evolving field of NMR. Key figures in addition to the Varian brothers were James N. Shoolery, Emery Rogers, Forrest Nelson, Martin E. Packard, and Weston A. Anderson.[5]

In 1956 Perkin–Elmer introduced a low-resolution, broad-line spectrometer. This model, however, was quickly discontinued and Varian then held a virtual monopoly in high-resolution NMR until September 1966 when JEOL (a Japanese corporation) introduced their model C60H. In April 1967 Perkin–Elmer introduced their model R20, and in 1968 Brucker Magnetics entered the field by introducing their model HX60. Varian and Brucker Magnetics are now the industry leaders. JEOL is third.

Notes

1. F. Bloch, "Nuclear Induction," *Physical Review* 70, nos. 7–8 (1–15 October 1946): 460–74.
2. W. G. Proctor and F. C. Yu, "The Dependence of a Nuclear Magnetic Reso-

nance Frequency upon Chemical Compound," *Physical Review* 77, no. 5 (March 1950): 717.

3. W.C. Dickinson, "Dependence of the F^{19} Nuclear Resonance Position on Chemical Compound," *Physical Review* 77 (1 March 1950): 736–37.

4. H. S. Gutowsky and R. E. McClure, "Magnetic Shielding of the Proton Resonance in H_2, H_2O, and Mineral Oil," *Physical Review* 81, no. 2 (15 January 1951): 276–77.

5. F. Bloch, Professor of Physics, Stanford University, Dr. Emery Rogers, Hewlett-Packard Corp., and J. N. Shoolery and W. A. Anderson, both of Varian Assoc., telephone interviews, 1974.

Spinning of a Nuclear Magnetic Resonance Sample

Samples placed in a nuclear magnetic resonance spectrometer are subjected to a strong magnetic field. From a theoretical understanding of the NMR phenomenon, it was known by both NMR spectrometer users and personnel of the then-only manufacturer of NMR equipment (Varian Associates, Palo Alto, California) that increased homogeneity of the magnetic field would allow NMR equipment to produce more detailed spectra. Physical spinning of the sample within the spectrometer, the innovation being described here, is one way to improve the effective homogeneity of the field. Spin is achieved by linking a small electric motor or air turbine to an appropriately designed sample holder.

Development History

Felix Bloch (the discoverer of the NMR phenomenon) suggested rapid sample spinning as one means of improving effective magnetic field homogeneity and, thus, the resolution of NMR spectra.[1] Two of Bloch's students, W. A. Anderson and J. T. Arnold, built a prototype spinner and experimentally demonstrated the predicted result.[2]

Commercialization

Varian engineers went to Bloch's laboratory, examined his prototype sample spinner, developed a commercial model, and introduced it into the market by December 1954. The connection between Bloch and Varian was so good and Varian's commercialization of the improvement so rapid that there was little time for other users to construct homebuilt spinners prior to that commercialization.

Notes

1. F. Bloch, "Line-Narrowing by Macroscopic Motion," *Physical Review* 94, no. 2 (15 April 1954): 496–97.

2. W. A. Anderson and J. T. Arnold, "A Line-Narrowing Experiment," *Physical Review* 94, no. 2 (15 April 1954): 497–98.

Pulsed NMR Spectrometer

Applying magnetic pulses rather than a steady magnetic field to samples being analyzed in an NMR spectrometer allows one to examine molecular dynamics. Among the phenomena made accessible to observation by the technique are rates of reaction and molecular relaxation times.

Development History
The spin echo phenomenon underlying pulsed NMR was discovered—and patented—in 1950 by E. L. Hahn, Professor of Physics at the University of Illinois.[1] Numerous authors explored and refined its application to NMR over the succeeding years.[2] Some 12 users built their own equipment in the years before equipment embodying it was commercially available.

Commercialization
Interviewees at Varian say that the firm did produce "one or two" pulsed NMRs in 1954 but then did not pursue commercialization further. The Harvey Wells Corporation was the first to make a significant commercialization effort: They brought their ELH spin echo system to market in May 1964.

Professor John S. Waugh of MIT was reportedly responsible for kindling the interest of the Harvey Wells Corporation in pulsed NMR. He had come to know the company through purchasing their magnets to build his own pulsed NMRs. Waugh told the Harvey Wells Corporation of the concept and suggested they license Hahn's patent—which they did. Hahn and Waugh both consulted for Harvey Wells and aided their effort to develop a commercial device.[3] Pulsed NMR was next commercialized by NMR Specialties and Brucker Magnetics, both in 1962.

Notes

1. E. L. Hahn, "Spin Echoes," *Physical Review* 80, no. 4 (18 November 1950): 580–94.
2. See H. Y. Carr and E. M. Purcell, "Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments," *Physical Review* 94, no. 3 (1 May 1954): 630–38; see also M. Sasson, A. Tzalmona, and A. Loewenstein, "A Spin Echo Attachment to Varian HR60 Nuclear Magnetic Resonance Spectrometer," *Journal of Scientific Instruments* 40 (1963): 133–34.
3. John S. Waugh, Professor of Chemistry, MIT, conversation at MIT, Cambridge, Mass., 1975.

Fourier Transform/Pulsed NMR

Fourier transform/pulsed NMR was an innovation applicable to the same analyses of molecular structure as conventional high-resolution NMR, but it offered an improvement in sensitivity of two orders of magnitude. The innovation was accomplished by coupling a computer capable of performing a fast Fourier transform algorithm directly to an NMR spectrometer.

Development History
Fourier transform/pulsed NMR was developed by R. R. Ernst and W. A. Anderson, two very creative researchers working at Varian Associates, a manufacturer of NMR spectrometers. They published their concept in 1966.[1] Development of a form of Fourier transform that was susceptible to rapid computation—a fast Fourier transform—by J. W. Cooley and J. W. Tukey in 1967[2] made the concept commercially feasible using the computers of the day. The product was developed in-house at Varian. Ernst and Anderson did not utilize the help of outsiders in their development work, but they were aware that other user and commercial groups were probably working on similar projects at the same time.

Commercialization

In July 1969 Varian reached the commercialization stage with the Ernst and Anderson project and introduced a Fourier transform accessory for its HA line of NMR spectrometers. This accessory was to be used in conjunction with an IBM 7090 computer. It was quickly followed by Digilab, which introduced an accessory in October 1969. Other quick commercializers were: Fabri-tek Instruments in February 1970, with a system based on a DEC PDP 8 computer; Brucker Magnetics in October 1970; and JEOL in 1971, with the PS–100 spectrometer with integrated computer.

Notes

1. R. R. Ernst and W. A. Anderson, "Application of Fourier Transform Spectroscopy to Magnetic Resonance," *Review of Scientific Instruments* 37, no. 1 (January 1966): 93–102.
2. William T. Cochran et al., G-AE Subcommittee on Measurement Concepts, "What Is the Fast Fourier Transform?" *IEEE Transactions on Audio and Electroacoustics* Au–15, no. 2 (June 1967): 45–55.

Heteronuclear Spin Decoupling

Heteronuclear spin decoupling is most useful for NMR spectroscopy work involving carbon 13 (C^{13}). Organic molecules have carbon as a "skeleton" with protons attached to them. This results in a very complicated NMR spectrum that can be simplified by heteronuclear spin decoupling.

Heteronuclear spin decoupling involves observing the C^{13} spectrum while irradiating the protons with a noise source tuned to their resonant frequency. This destroys the coupling of the protons to the C^{13} spectrum and thus makes that spectrum simpler. It also makes the C^{13} spectrum stronger (Overhauser effect), in effect increasing the sensitivity of the instrument in this application.

Development History

Double irradiation, the phenomenon at the base of heteronuclear spin decoupling, was first suggested by Felix Bloch in 1954. This basic idea was jointly developed and tested by Bloch with Martin E. Packard and James N. Shoolery at Varian Associates. The patent on the innovation is held by all three. In 1955 Arnold L. Bloom (also of Varian) and Shoolery published a simplification of the technique.[1]

Commercialization

Felix Bloch, Professor of Physics at Stanford University, and Varian Associates already had a close relationship established at the time of this innovation. In 1958 Varian commercialized a heteronuclear spin decoupler accessory. In 1960 Varian discontinued this accessory, and in 1962 they allowed a field engineer for Varian, a Mr. Yeiko, to offer the accessory in a new company he was founding, NMR Specialities. In 1962 Perkin–Elmer offered the capability. In 1964 Varian reintroduced the heteronuclear spin decoupling capability on its HA line of spectrometers. In 1966 JEOL (a Japanese corporation) offered it on its C60H model and in 1968 Brucker Magnetics offered it on their HF and HX series NMR spectrometers.

Note

1. Arnold L. Bloom and James N. Shoolery, "Effects of Perturbing Radiofrequency Fields on Nuclear Spin Coupling," *Physical Review* 97, no. 5 (1 March 1955): 1261–65.

Homonuclear Spin Decoupling

Homonuclear spin decoupling is used in proton spectroscopy. It allows one to associate particular lines in the spectrogram with particular protons. It is accomplished by irradiating one specific proton line while observing another proton line or group of lines. If irradiating the former affects the latter, then one knows that the two lines are closely related. If they were not, they would not display this coupling behavior.

Development History

Homonuclear spin decoupling goes back, as does heteronuclear spin decoupling, to a suggestion by Felix Bloch in 1954. W. A. Anderson of Varian Associates, however, was the first to demonstrate homonuclear decoupling of protons.[1] In 1959 Junkichi Itoh and Siro Sato[2] published a modification of the technique that considerably simplified the equipment required.

Commercialization

In 1964 Varian introduced homonuclear spin decoupling as an accessory on its HA60 and NMR spectrometer. James N. Shoolery of Varian estimates that between one- and two-dozen homemade versions of homonuclear spin decouplers were in use by users prior to commercialization. In 1967 Perkin–Elmer introduced homonuclear spin decoupling on its R20 NMR. In 1964 Brucker introduced it on its HX60 and JEOL introduced it on its C60 HL. In 1969 Varian introduced the innovation on its XL100 NMR spectrometer.

Notes

1. Weston A. Anderson, "Nuclear Magnetic Resonance Spectra of Some Hydrocarbons," *Physical Review* 102, no. 1 (1 April 1956): 151–67.
2. Junkichi Itoh and Siro Sato, "Double Proton Magnetic Resonance by a Side Band Method," *Journal of the Physical Society of Japan* 14 (1959): 851–52.

Frequency Synthesizer

The NMR spectrometer requires a very stable frequency source to operate properly. The most stable frequency sources commonly used in science incorporate quartz crystal references. Prior to the development of the frequency synthesizer, quartz crystal references were only available in the form of single-frequency oscillators. Each time one wanted to change frequencies, one had to change oscillators. The frequency synthesizer allows one to dial in on any frequency one wants with quartz stability—a major convenience for users.

Development History

Frequency synthesizers existed as commercial products prior to their application to NMR spectrometers by spectrometer manufacturers. Users who wished to have this feature on their NMRs simply purchased a synthesizer and wired it into their equipment appropriately.

Commercialization

In 1968 Brucker was the first to offer a frequency synthesizer built into their B–KR321S and B–KR322S models of NMR spectrometers. In September 1969 Varian offered a frequency synthesizer in their XL100 NMR spectrometers.

Superconducting Solenoids

The performance of NMR spectrometers improves as the magnetic field strength applied to the sample being analyzed is increased. Higher field strength increases both sensitivity and resolution of the instrument. Superconducting solenoids are capable of reaching significantly higher field strengths in the NMR application than are iron magnets. They are, however, somewhat less convenient to use as they must be cooled to liquid helium temperature for operation.

Development History

The NMR spectrometer with superconducting magnets was developed at Varian Associates, manufacturers of NMR spectrometers. Varian was induced to undertake the project by Bill Phillips of Du Pont. Phillips said that if Varian would build a superconducting NMR, Du Pont would place an order and provide some development money. Varian's development work involved research on field homogeneity, probe design for use with superconductors, and magnetic shielding as well as work on the superconducting magnets themselves.[1]

Commercialization

Varian introduced the NMR spectrometer with superconducting magnets in March of 1964. In February of 1965 Magnion offered a superconducting instrument appropriate for applications in which field homogeneity was not critical. In 1966 Varian introduced the HR–220 with a superconducting magnet system, and in 1971 Brucker introduced a superconducting magnet system.

Note

1. F. A. Nelson and H. E. Weaver, "Nuclear Magnetic Resonance Spectroscopy in Superconducting Magnetic Fields," *Science* 146 (9 October 1964): 223–32.

Shim Coils

To achieve high-quality NMR spectra it is important to subject the sample to a homogeneous magnetic field. Shim coils are a means of improving the homogeneity of the magnetic field. They consist of small electromagnetic coils attached to each pole face of the primary magnetics of the NMR spectrometer. The current flowing through these shim coils is carefully adjusted to correct any inhomogeneities detected in the magnetic field affecting the samples.

Development History

J. T. Arnold of Varian Associates was the first to propose the use of shim coils in NMR.[1] His paper appeared in 1956. In 1958 M. Golay, a scientist employed in Perkin–Elmer Corporation, another manufacturer of NMR spectrometers, published an improved shim coil design.[2] In 1959 H. Primas, Professor of Physics at the Swiss Federal Research Institute and a user of NMR, also published an article on shim coils.[3]

Commercialization

As far as we can determine, a Swiss firm, Trub–Tauber & Cie located in Zurich, was the first to commercialize NMR spectrometers with a shim coil, apparently in 1958.[4] Trub–Tauber & Cie obtained their design for shim coils from Professor Primas, an established consultant to that firm. Primas used NMR in his work and also was involved in designing NMR equipment. Varian Associates commercialized shim coils about 1960. In January 1966 Varian introduced a more sophisticated version of shim coils, Auto shim, on their HA100 model NMR spectrometer.

Notes

1. James T. Arnold, "Magnetic Resonances of Protons in Ethyl Alcohol," *Physical Review* 102, no. 1 (1 April 1956): 136–50.
2. Marcel J. E. Golay, "Field Homogenizing Coils for Nuclear Spin Resonance Instrumentation," *Review of Scientific Instruments* 29, no. 4 (April 1958): 313–15.
3. H. Primas, R. Arndt, and R. Ernst, *Zeitschrift für Instrumentenkunde* 67 (1959): 295.
4. Charles A. Reilly, "Nuclear Magnetic Resonance Spectrometry," *Review of Fundamental Developments in Analysis* 30, no. 4 (April 1958): 839–48.

Primas Polecaps

Primas polecaps are yet another means of improving homogeneity of magnetic field strength in the sample cavity of an NMR. The Primas design has the virtue of being of value for differing field strengths instead of being optimized for a particular field strength.

Development History

Primas polecaps are based on an idea by H. Primas, Professor of Physics at the Swiss Federal Research Institute. Primas was a user of NMR and also a consultant at Trub–Tauber & Cie, a manufacturer of NMR spectrometers.

Commercialization

In his role as consultant to Trub–Tauber & Cie, Primas transferred the design for Primas polecaps to that firm. When Brucker Magnetics, another manufacturer of NMR, acquired Trub–Tauber & Cie around 1964, they also acquired information regarding the Primas polecap design. Brucker commercialized these polecaps in 1968.

Field Frequency Lock

A field frequency lock keeps the ratio between the magnetic field and the radio frequency of an NMR spectrometer constant. The lock produces precisely correct spacing of absorption lines, which in turn allows exact superposition of sequential spectra for a given sample because, for each pass, the spectral lines are exactly aligned. This allows time-averaging experiments to improve signal-to-noise ratios when the signal is very weak. It therefore allows investigation of dilute samples and rare molecules.

Development History

After 1948 users of NMR knew that one could in principle build field frequency locks.[1] Since most users were chemists rather than electrical engineers, few actually did build such locks prior to the commercialization of the innovation. One of the users who did build such a lock was Saul Meiboom at Bell Laboratories.

Commercialization

In 1961 Varian Associates offered an external field frequency lock on their A60 and

NMR model. (An external field frequency lock is one in which the magnetic field sensing device is not quite in the same position as the sample. An internal field frequency lock is one in which the sensing device for the magnetic field is in the sample chamber itself.) In 1962 W. A. Anderson of Varian wrote an article on an internal field frequency lock control system,[2] and in February 1964 Varian was the first to commercialize an internal field frequency lock. In September 1966 JEOL (a Japanese corporation) offered both internal and external locks on their C60H NMR spectrometer. In July 1968 Brucker Magnetics commercialized internal and external field frequency locks on their HF60 model.

Notes

1. Martin E. Packard, "A Proton-Controlled Magnetic Field Regulator," *Review of Scientific Instruments* 19, no. 7 (July 1948): 435–39.

2. Weston A. Anderson, "Applications of Modulation Techniques to High Resolution Nuclear Magnetic Resonance Spectrometers," *Review of Scientific Instruments* 33, no. 11 (November 1962): 1160–66.

T_1rho

The T_1rho is used to measure slow motion in semisolids by measuring relaxation time. Earlier approaches to measuring slow motion involved lowering the magnetic field of the NMR instrument, but this caused signal-to-noise problems. The approach of the T_1rho accessory is to lower the amplitude of the radio frequency field. The radio frequency field then becomes the energy source that the material absorbs to relax. Maintaining high magnetic field strength during this process retains the high sensitivity of the NMR spectrometer.

Development History

T_1rho experiments were first done by physicists at the University of Illinois in a group working under Charles P. Slichter.[1] Numerous other groups did work on the problem over the next 10 years.[2] Although the original work was done on metal samples, interest grew among people doing research on biological materials and polymers.

Commercialization

In 1953 the T_1rho accessory was commercialized by Brucker Magnetics. As far as can be determined, the Brucker development group obtained the information they needed from published documents rather than through consultation with the developers of the technology.

Notes

1. Charles P. Slichter and David Ailion, "Low-Field Relaxation and the Study of Ultraslow Atomic Motions by Magnetic Resonance," *Physical Review* 135, no. 4A (17 August 1964): A1099–1110.

2. Brian D. Sykes and John M. Wright, "Measurement of Nuclear Spin Relaxation Times on an HA-100 Spectrometer," *Review of Scientific Instruments* 41, no. 6 (June 1970): 876–77. (These Harvard University authors describe modification of a Varian HA100 for the performance of T_1rho experiments.)

Pulsed Field Gradient Accessory

The pulsed field gradient accessory measures diffusion coefficients in semiliquid or liquid samples. It is an improvement on the pulsed NMR spin echo technique (see above). It involves reducing the field gradient during the times at which the radio frequency pulses are being applied to the sample and also at the time of appearance of the echo. This results in a broad echo that can be measured more accurately. The technique allows a one or two order-of-magnitude improvement in the accuracy of measurement of diffusion coefficients.

Development History

The pulsed field gradient accessory was developed by E. O. Stejskal and J. E. Tanner, researchers in the Department of Chemistry at the University of Wisconsin.[1] These authors had been using the spin echo method of E. L. Hahn[2] as developed by H. Y. Carr and E. M. Purcell.[3] Stejskal and Tanner were motivated to develop the pulsed field gradient accessory to eliminate some experimental limitations that they found in the spin echo method. Important precursors to their work were that of A. G. Anderson et al.[4] who noted diffusion in field gradients as well as that of D. W. McCall, D. C. Douglass, and E. W. Anderson[5] who noted the experimental possibilities of this technique in measuring self-diffusion coefficients. The basic apparatus used by Stejskal and Tanner[6] closely resembles that described by J. C. Buchta, H. S. Gutowsky, and D. E. Woessner earlier.[7]

Commercialization

The pulsed field gradient accessory was first commercialized by Brucker Magnetics. Brucker apparently acquired the information they needed to commercialize the unit from publications and conferences rather than consultants. Stejskal himself was not contacted by Brucker for help with the design.[8]

Notes

1. E. O. Stejskal and J. E. Tanner, "Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient," *Journal of Chemical Physics* 42, no. 1 (1 January 1965): 288–92.
2. E. L. Hahn, "Spin Echoes," *Physical Review* 80, no. 4 (18 November 1950): 580–94.
3. H. Y. Carr and E. M. Purcell, "Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments," *Physical Review* 94, no. 3 (1 May 1954): 630–38.
4. A. G. Anderson et al., "Spin Echo Serial Storage Memory," *Journal of Applied Physics* 26, no. 1 (November 1955): 1324–38.
5. David W. McCall, Dean C. Douglass, and Ernest W. Anderson, "Self-Diffusion Studies by Means of Nuclear Magnetic Resonance Spin-Echo Techniques," *Deutsche Berichte der Bunsen-Gesellschaft für Physikalische Chemie* 67, no. 3 (1963): 336–40.
6. E. O. Stejskal, "Use of an Analog-to-Digital Converter in Pulsed Nuclear Resonance," *Review of Scientific Instruments* 34, no. 9 (September 1963): 971–75.
7. J. C. Buchta, H. S. Gutowsky, and D. E. Woessner, "Nuclear Resonance Pulse Apparatus," *Review of Scientific Instruments* 29, no. 1 (January 1958): 55–60.
8. E. O. Stejskal, Department of Chemistry, University of Wisconsin, telephone interview, 1975.

Electronic Integrator

The electronic integrator integrates the area under the peaks of the NMR spectrometer spectrum. This area is proportional to the total number of protons contributing to that peak. It allows a much more accurate count of this number than was possible previously.

Development History

Integrators are used for a range of purposes in scientific research and were available as modules in the commercial marketplace prior to their commercialization as a built-in feature of an NMR spectrometer. Interested users could purchase these units and wire them into their equipment if they so desired. Among the users who did this were people such as Baker at Dow Chemical Research.[1]

Commercialization

J. N. Shoolery and W. A. Anderson were the researchers at Varian Associates who developed that firm's electronic integrator. Varian offered it as an accessory in 1960. In 1961 the Varian model A60 and NMR spectrometer had a built-in integrator. In 1965 JEOL offered an electronic integrator.[2]

Notes

1. J. N. Shoolery, Varian Associates, Palo Alto, Calif., telephone interview, 1975.
2. W. A. Anderson, Varian Associates, Palo Alto, Calif., telephone interview, 1975.

Multinuclei Probe

The multinuclei probe allows a user to examine any of more than 70 nuclei types without changing any hardware. The major advantage this innovation presents to users relative to old-style probes can be appreciated when one understands that such probes were restricted to the examination of only a single nucleus type and cost several thousand dollars each. Also, the time involved in changing from one probe to another could take several hours.

Development History

The multinuclei probe was developed by Daniel Traficante, a visiting scientist in MIT's Department of Chemistry, and by Michael Mulcay, president of United Development Corporation in Lexington, Massachusetts. The two lived in the same town and knew each other socially. One day Traficante told Mulcay, an electronics engineer, about his idea for a multinuclei probe, and they decided to get together to work on it. The first probe they developed was installed at MIT in 1972. The second was installed at Michigan State University in 1974; one was also installed in Australia in 1974. All of these multinuclei probes were built and installed by Traficante and Mulcay according to a design they published in September 1974.[1]

Commercialization

Interest in multinuclei probes on the part of users apparently stimulated Varian Associates to develop their own multinuclei probe in cooperation with Paul Ellis of the University of South Carolina. This probe design was commercialized in 1974. In late

1974 Brucker Magnetics commercialized a multinuclei probe of the Traficante and Mulcay design. The arrangement at that time was that Brucker would supply Traficante and Mulcay with parts and components and that those two would build the probes and would sell them back to Brucker for marketing.

Note

1. Daniel D. Traficante, James A. Simms, and Michael Mulcay, "An Approach to Multinuclei Capability in Modern NMR Spectrometers," *Journal of Magnetic Resonance* 15 (September 1974): 484–97.

Proton-Enhanced Nuclear Induction Spectroscopy

Proton-enhanced nuclear induction spectroscopy allows the examination of the molecular structure of molecules that either are naturally rare or that have extremely small magnetic moments. When a nucleus is rare, the signal is weak. The normal solution to weak signals (time averaging) cannot be used here because the relaxation times of the spins are too long. That is, the spin takes too long to recover its original polarization, which is lost during an observation—the relaxation time may be one hour. The proton-enhanced nuclear induction spectroscopy method solves this problem by replenishing the polarization of the rare spins from the abundant spins rather than in the usual way through the lattice. This makes use of the coupling between rare and abundant spins in the way proposed by S. R. Hartmann and E. L. Hahn.[1] One establishes the coupling by double resonance and polarizes the rare spins in (perhaps) a millisecond. In effect, one pumps the polarization of the abundant spins out through the rare spins and thus elicits their spectra. The abundant spins are usually protons.[2]

Development History

S. R. Hartmann and E. L. Hahn, Department of Physics, University of California, Berkeley, introduced the double resonance method in 1962. F. M. Lurie and C. P. Slichter, University of Illinois, performed a double resonance experiment on lithium metal and carried it further in 1964.[3] In 1965 R. Freeman and W. A. Anderson published their experiments with double resonance that used modulated perturbing radio frequency fields.[4]

Commercialization

Brucker Magnetics was induced to work on commercializing proton-enhanced nuclear induction spectroscopy by John S. Waugh, Professor of Chemistry, MIT. Waugh was a consultant to Brucker. Varian Associates also initiated work on the technique by 1973.

Notes

1. S. R. Hartmann and E. L. Hahn, "Nuclear Double Resonance in the Rotating Frame," *Physical Review* 128, no. 5 (1 December 1962): 2042–53.
2. John S. Waugh, Professor of Chemistry, MIT, conversation at MIT, Cambridge, Mass., 1974.
3. Fred M. Lurie and Charles P. Slichter, "Spin Temperature in Nuclear Double Resonance," *Physical Review* 133, no. 4A (17 February 1964): A1108–22.
4. R. Freeman and W. A. Anderson, "Nuclear Magnetic Double Resonance. Transmission of Modulation Information Through the Nuclear Spin-Spin Coupling," *Journal of Chemical Physics* 42, no. 4 (15 February 1965): 1199–1229.

THE TRANSMISSION ELECTRON MICROSCOPE (TEM)

The First Electron Microscope

The electron microscope is the electronic analog to the optical microscope. The conventional optical microscope uses glass lenses to bend and focus beams of light to create an enlarged image of a sample. Analogously, the electron microscope uses magnetic and electric fields to bend a beam of electrons to achieve an enlarged image of a sample. Because the wavelength of electrons is more than 1000 times shorter than the wavelength of light used in conventional light microscopy, the electron microscope can achieve 1000 times greater resolution than can the light microscope. Although the optical microscope is limited in resolution to about 1000 angstroms (Å), the resolution of a modern electron microscope can be on the order of 1Å.

The very great improvement in resolving power offered by the electron microscope over the best previously available optical microscopes made it enormously important to researchers in many fields, ranging from metallurgy to biology.

Development History

The first work in the electron microscope was done at the Technische Hochschule in Berlin by Max Knoll and his student Ernst Ruska. These two were working on high-speed oscilloscopes for the purpose of building devices capable of measuring the effects of lightning more effectively.[1] Their investigations of the optics of electrons in a vacuum led to their development of the electromagnetic lens, a key element in the electron microscope. In 1931 they reported their observation of the enlargement of the images of apertures.[2]

A few days after Knoll reported his initial results, G. R. Rudenberg, an employee of Siemens, a German electrical manufacturer, applied for a patent on the theory of the electron microscope.[3] The close timing of these two events plus the apparent lack of prior work on the part of Rudenberg that could be logically linked to an electron microscope caused some skepticism regarding the source of his insight. Rudenberg's patent covered the basic use of magnetic and electrostatic lenses to form electrooptical instruments in which electrons took the same part as light does in light optics. Also in 1931 E. Bruche (of the German firm AEG) published a report of work in electron optics.[4] By 1932 Knoll and Ruska had built an improved electron microscope that operated with an electron beam of 65 kv and reached 120 times magnification.[5]

L. Marton, a researcher in Belgium, had read some of Knoll and Ruska's early papers and started to build his own electron microscope in 1932. Marton focused on the problem of preparing samples to be observed under the electron microscope, especially biological samples. It had early been thought that an electron beam would destroy biological samples, but Marton demonstrated that, indeed, they could be prepared and examined.[6]

In 1933 Knoll and Ruska had improved their electron microscope to the point that it was able to exceed the resolution of an optical microscope. Biologists and chemists at the Technische Hochschule in Berlin made use of this microscope and became very interested in its possibilities. In 1935 Marton built an electron microscope that was able to exceed the resolution of an optical microscope by a factor of 10.

Commercialization

In 1937 Ruska and B. von Borries were hired by Siemens to develop an electron microscope for production. They had a prototype ready by the end of 1938, and in 1939

Siemens started production of commercial electron microscopes. In total, Siemens produced about 30 units during 1939 and the early war years.[7] In 1938 Marton left Europe to come to RCA in the United States, and he brought along with him an electron microscope of his own design.[8] In 1940 RCA also hired J. Hillier, another early researcher in electron microscopy. Before the end of 1941 Marton left RCA for Stanford University. In 1941 RCA commercialized a microscope of Hillier's design, which was known as the RCA Type B or the EMB.

Notes

1. Martin M. Freundlich, "Origin of the Electron Microscope," *Science* 142, no. 3589 (11 October 1963): 185–88.
2. L. Marton, *Early History of the Electron Microscope* (San Francisco: San Francisco Press, 1968), 5.
3. T. Mulvey, "Origins and Historical Development of the Electron Microscope," *British Journal of Applied Physics* 13 (1962): 197–207.
4. Marton, *Early History of the Electron Microscope,* 19.
5. Mulvey, "Origins and Historical Development of the Electron Microscope," 200–1.
6. Marton, *Early History of the Electron Microscope,* 19–22; and Mulvey, "Origins and Historical Development of the Electron Microscope," 202–4.
7. Mulvey, "Origins and Historical Development of the Electron Microscope," 206; and Ralph W. G. Wyckoff, *Electron Microscopy: Technique and Applications* (New York: Interscience, 1949), 14.
8. Marton, *Early History of the Electron Microscope,* 35.

Pointed Filaments

The electron microscope operates by accelerating a beam of electrons. The coherence of this beam of electrons is very important to achieving high resolution in the electron microscope, especially in the region below 8 Å resolution. The source of electrons in an electron microscope is a filament much like the filament in an electric light bulb. It was found that making this filament in a pointed shape greatly improved the coherence of the electron microscope beam.

Development History

Pointed filaments were developed in the early 1960s by H. Fernandez-Moran, a biologist at the University of Chicago.[1]

Commercialization

Various versions of pointed filaments were commercialized in the late 1960s by two firms that specialized in electron microscope accessories and supplies. These two firms were the C. W. French Company and the Ladd Company. We have little information on how these firms got involved in the production of pointed filaments. Ladd reported[2] that he visited the Fernandez-Moran laboratory and observed the fabrication of pointed filaments there.

Notes

1. T. Hibi, "Operating Condition of Point Cathode and Resolution of Electronmicroscope," in *Electron Microscopy 1964* (Proceedings of the Third European Regional Conference, Prague, 26 August–3 September 1964), ed. M. Titlbach, Vol. A

(Prague: Publishing House of the Czechoslovak Academy of Sciences, 1965), 121–22; H. Fernandez-Moran, "Applications of Improved Point Cathode Sources to High Resolution Electron Microscopy," in *Electron Microscopy 1966* (Sixth International Congress for Electron Microscopy, Kyoto, Japan, 28 August–4 September 1966), Vol. 1: *Non-Biology,* ed. Ryozi Uyeda (Tokyo: Maruzen, 1966), 27–28.

2. Mrs. Margaret Ladd, Burlington, Vt., telephone interview, 1974; C. W. French, Agawam, Mass., telephone interview, 1974.

Telefocus Electron Gun

The telefocus gun was a magnetic and electronic innovation that allowed the user of an electron microscope to separately control the diameter and the intensity of the electron beam of an electron microscope. Separate control of these functions is important to users, but they had been inherently linked in earlier gun designs.

Development History

The telefocus gun was designed by K. H. Steigerwald, a researcher at the Max Planck Institute in Germany.[1] Steigerwald reported his development in 1949. His design was quickly replicated by several metallurgists who had great need for it in their studies that required the use of the electron microscope.

Commercialization

Steigerwald was a consultant for Siemens, a German producer of electron microscopes. Siemens introduced the telefocus design in 1951. In the late 1950s Philips Corporation, Eindhoven, the Netherlands, commercialized it, and in 1965 RCA started selling a kit to retrofit their existing microscopes with the innovation.

Note

1. K. H. Steigerwald, "Ein Neuartiges Strahlerzeugungs-System für Elektronenmikroskope," *Optik* 5, no. 8/9 (1949): 469–78.

Double Condenser Lens

The double condenser lens replaces a single condenser lens in the optical system of an electron microscope. This substitution provides the user with several important improvements. First, the intensity of the electron beam can be varied over a wider range. This permits a greater range of specimen-viewing conditions for users: Strong illumination is possible for thick specimens, weak illumination is possible for delicate specimens. Second, the double condenser lens creates more working space between the condenser and objective lenses. This is the space in which users place their sample. The increase in space allows users to design accessories for handling samples with greater freedom. Finally, the double condenser lens enables users to reduce the area of their sample that is exposed to the electron beam. This in turn allows users to reduce specimen damage of delicate specimens.

Development History

L. Marton claims that he developed the double condenser lens at Stanford University in the 1940s.[1] It is possible that this was also done independently by other users since double condenser lenses were also a feature of optical microscopes and the analogy was clear.

Commercialization

The double condenser lens was first offered commercially by Siemens about 1952.[2] Several other microscope makers quickly followed, but RCA delayed until 1959, when they introduced a double condenser retrofit kit for their EMU3 electron microscope.[3]

Notes

1. L. Marton, *Early History of the Electron Microscope* (San Francisco: San Francisco Press, 1968), 41; also L. Marton, "A 100-kv Electron Microscope," *Journal of Applied Physics* 16 (March 1945): 131–38.
2. B. v. Borries, "The Physical Situation and the Performance of High-Resolving Microscopy Using Fast Corpuscles," in *Proceedings of the Third International Conference on Electron Microscopy, London 1954* (London: Royal Microscopical Society, 1956), 4–25, esp. 4 and Plate V.
3. John Coleman, former employee of RCA's Electron Microscope Division, conversations at MIT, Cambridge, Mass., 1974.

Correction of Astigmatism in the Objective Lens

Electron microscope lenses are subject to imperfections (e.g., astigmatism) just as optical lenses are. Astigmatism in the objective lens is the result of imperfections in the pole piece of the electromagnet used in that lens.

Development History

Many users were trying to improve the resolution of their microscopes by (among other things) polishing, boring, and mechanically adjusting the pole pieces of their objective lenses in order to eliminate astigmatism.[1]

Commercialization

The first to commercialize an adjustable astigmatism corrector for an objective lens was RCA on their advanced EMU model in 1947. The correction was achieved by eight screws built into the objective pole piece. This commercial version was developed by J. Hillier and E. G. Ramberg at RCA.[2]

Notes

1. Dr. John Riesner, RCA Sarnoff Laboratories, conversations at Cherry Hill, N.J., 1974.
2. James Hillier, "Further Improvement in the Resolving Power of the Electron Microscope," *Journal of Applied Physics* 17 (April 1946): 307–9; also James Hillier and E. G. Ramberg, "The Magnetic Electron Microscope Objective: Contour Phenomena and the Attainment of High Resolving Power," *Journal of Applied Physics* 18 (January 1947): 61–71.

Well-Regulated High-Voltage Power Supplies

Electron microscopes require high voltages to operate. A very high stability in the high-voltage supply of an electron microscope is a well-known prerequisite for achieving high resolution.

Development History

The first electron microscope and the first few precommercial replications used batteries connected in series to supply the high voltages required. A very stable high voltage could be obtained by this means, but the major inconvenience associated with this solution can be readily imagined: voltages on the order of 80,000 v were needed—supplied by nearly 40,000 single wet-cell batteries connected in series. A visitor to the laboratory of L. Marton, an early and outstanding experimenter in electron microscopy, recalls an entire room filled with batteries on floor-to-ceiling racks with a full-time technician employed to maintain them. The first commercial electron microscope, built by Siemens in Germany in 1939, substituted a power supply for the batteries but could not make its output voltage as constant as could be done with the batteries.[1]

Commercialization

When RCA decided to build an electron microscope, an RCA electrical engineer, Jack Vance, undertook to build a highly stable power supply and by several inventive means achieved a stability almost good enough to eliminate voltage stability as a constraint on the performance of a high-resolution microscope. Vance achieved this by using radio frequency rather than line-voltage frequency to actuate the high-voltage rectifier tubes in the power supply and by incorporating a reference battery in a feedback circuit to stabilize the high voltage.[2]

Vance's innovative power supply was commercialized in 1941 in RCA's first-produced electron microscope, the RCA Type B (EMB).

Notes

1. Ralph W. G. Wyckoff, *Electron Microscopy: Technique and Applications* (New York: Interscience, 1949), 16.
2. A. W. Vance, "Stable Power Supplies for Electron Microscopes," *RCA Review* 5, no. 3 (January 1941): 293–300.

Regulated Lens Power Supply

The lenses of electron microscopes are electromagnets. To provide a steady magnetic field they require a very stable supply of electric current. This current is provided by the lens power supply. Early electron microscopes built by users and the early Siemens's commercially produced electron microscope used batteries in conjunction with water cooling as their lens power supply system. The batteries supplied the current necessary, while the water cooling prevented the resistance in the lens wiring from changing with temperature, thus changing current flow in the lens magnetic field. As can be imagined, both the batteries and the water cooling contributed significantly to the cumbersomeness and expense of the early electron microscopes.

Development History

Jack Vance of RCA eliminated both the need for batteries and the need for water cooling in the lens power supply he designed. He replaced the high-current, low-voltage battery supply with a low-current, high-voltage supply from a regulated power supply and designed a current regulator into this power supply, so that changes in temperature of the lens windings would not affect lens performance.[1]

Commercialization

The regulated lens power supplies designed by Vance were commercialized in the RCA Type B (EMB) electron microscope introduced commercially in 1941.

Note

1. A. W. Vance, "Stable Power Supplies for Electron Microscopes," *RCA Review* 5, no. 3 (January 1941): 293–300.

Rubber Gasket Sealing of Vacuum System

The interior of an electron microscope is kept under a very hard vacuum. This is essential to its operation as electron beams cannot travel effectively in air. The electron microscope has many joints that are opened and closed frequently by the operator. In modern electron microscopes, rubber gaskets are used to make these joints airtight when they are closed.

Development History

Early electron microscopes used carefully machined surfaces covered with a special grease to achieve a vacuum-tight seal. Although this procedure had often been followed in high-vacuum work of the period, it proved very troublesome in the case of electron microscopy. Sealing grease from the joints infiltrated the vacuum chamber of the electron microscope, where it became charged by the electron beam. This charged material then distorted the electron beam in various unanticipated ways, destroying the microscope's performance. L. Marton realized the problem and designed rubber gaskets into the electron microscopes he built in the late 1930s.[1] However, Siemens's 1939 production unit—the first electron microscope commercialized—used machined surfaces and vacuum grease.

Commercialization

When Marton came to RCA in 1938, he carried with him one of his microscopes that used rubber gaskets to seal the vacuum system.[2] This feature was adopted for the RCA Type B (EMB) electron microscope commercialized in 1941.

Notes

1. L. Marton, *Early History of the Electron Microscope* (San Francisco: San Francisco Press, 1968), 22.
2. Ibid., 35.

Three-Stage Magnification

Creating a three-stage magnification system for the electron microscope involved inserting a third intermediate lens in the electron optical system. Three-stage magnification allowed users to adjust the magnification more widely. It thus allowed them to examine the total specimen at one time at a low magnification.

Development History

In 1944 an electron microscope containing three-stage magnification was built by J. B. le Poole, Director of the Institute for Electron Microscopy in Delft, the Netherlands. The microscope was used for a month and then taken apart and hidden from the German enemy until the end of the war. After the war it was described in a *Philips Technical Review*.[2] An electron microscope with three-stage magnification was also built by L. Marton at Stanford University in 1944.[3]

Commercialization
J. B. le Poole, designer of the electron microscope containing three-stage magnification, was a consultant to Philips Corporation in Eindhoven, the Netherlands. In 1947 Philips introduced commercially a 100 kv electron microscope patterned after the microscope built at Delft.

Notes

1. L. Marton, *Early History of the Electron Microscope* (San Francisco: San Francisco Press, 1968), 41.
2. J. B. le Poole, "A New Electron Microscope with Continuously Varying Magnification," *Philips Technical Review* 9, no. 2 (1947): 33–45.
3. "A New Electron Microscope for 100 kV," *Philips Technical Review* 9, no. 6 (1947): 179.

Scaled-up Objective Pole Piece

A pole piece is part of an electromagnetic lens like those used in electron microscopes. An objective pole piece is, therefore, part of the objective lens of the electron microscope. The innovation of enlarging the objective pole piece had several advantages over previous pole piece design. It reduced spherical aberration—a type of flaw in lens performance—and it increased intensity of the image. It also reduced the cost of producing the lens by reducing both the machining accuracy needed and the precision with which the pole piece must be aligned in the electron microscope.

Development History
The scaled-up objective pole piece was developed by L. Marton when he was at RCA in 1940.[1] He incorporated it in his model No. 4, which was also known as the RCA Type A. Marton, in his 1968 book on the early history of the electron microscope, reports that this innovation was partly inspired by two theoretical papers, one by R. Rebsch and W. Schneider and the other by W. Glaser.[2]

Commercialization
Although the scaled-up objective pole piece was developed at RCA, it was first commercialized by Metropolitan Vickers Electrical Company in 1949 in their model EM-3[3]; Philips followed in 1950.[4]

Notes

1. L. Marton, M. C. Banca, and J. F. Bender, "A New Electron Microscope," *RCA Review* 5, no. 2 (October 1940): 232–43.
2. L. Marton, *Early History of the Electron Microscope* (San Francisco: San Francisco Press, 1968), 38.
3. M. E. Haine, R. S. Page, and R. G. Garfitt, "A Three-Stage Electron Microscope with Stereographic Dark Field, and Electron Diffraction Capabilities," *Journal of Applied Physics* 21 (February 1950): 173–82.
4. A. C. van Dorsten, H. Nieuwdorp, and A. Verhoeff, "The Philips 100 kV Electron Microscope," *Philips Technical Review* 12, no. 2 (August 1950): 33–64.

Goniometer Specimen Stage

A specimen stage is a device used to mount specimens properly within the electron microscope. A goniometer stage is a device that can be tilted in one or two directions while it is in the microscope. This feature is useful in many instances and is necessary in certain materials science work.

Development History

The earliest microscope stages were simple screens upon which the sample to be observed was placed. As electron microscopes and microscopy matured starting in the early 1960s, users started to need stages that would allow them to observe their samples under various special conditions. U. Valdre was apparently either the first or among the first to develop goniometer type stages. He was a materials scientist at the University of Bologna and needed such a stage for his work.[1]

Commercialization

Siemens and Philips commercialized Valdre-type goniometer stages in the early 1960s. RCA commercialized such stages in 1964.

Note

1. U. Valdre, "A Universal Specimen Stage and Combined Cartridges for an Electron Microscope," in *Electron Microscopy 1966* (Sixth International Congress for Electron Microscopy, Kyoto, Japan, 28 August–4 September 1966), Vol. 1: *Non-Biology,* ed. Ryozi Uyeda (Tokyo: Maruzen, 1966), 165–66.

Cold Specimen Stage

A cold specimen stage is one that can keep samples cold while they are being examined under the electron microscope. Cooling can be achieved quite simply by thermally connecting the stage to a source of liquid nitrogen outside the electron microscope.

Development History

Cold stages were developed very early in the history of electron microscopes by L. Marton.[1] Both the microscope Marton brought to RCA when he became an employee and the one he developed at RCA had such stages.

Commercialization

In the mid-1950s Siemens was first to commercialize the cold stage.[2] In the mid-1960s demand for such stages began to pick up among biologists who were eager to reduce the radiation damage inflicted on their samples by electron microscopy.

Notes

1. L. Marton, "A New Electron Microscope," *Physical Review* 58 (1 July 1940): 57–60.
2. F. S. Sjöstrand and J. Rhodin, eds., *Electron Microscopy, Proceedings of the Stockholm Conference September 1956* (New York: Academic Press, 1957), 27.

High-Temperature Specimen Stage

A high-temperature stage can heat up to perhaps 3000°C—a very high temperature—while inside the microscope. It is important that the electron microscope be designed in such a way that the expansion of metals, and so on, associated with the high temperatures not deform the microscope or degrade its resolution.

Development History

The first high-temperature specimen stage was developed by M. von Ardenne, a researcher at an institute in Berlin.[1]

Commercialization

In the late 1950s metallurgists started to demand high-temperature stages from manufacturers. In 1965 (approximately) RCA commercialized such a stage.

Note

1. Abstract in V. E. Cosslett, ed., *Bibliography of Electron Microscopy* (London: Edward Arnold, 1950), 18.

Biased Electron Gun

The device in the electron microscope that generates the electron beam used for "seeing" the sample is called an electron gun. It is important to the performance and resolution capability of an electron microscope that the electron gun generate an intense, stable, and coherent electron beam. On all these dimensions, the biased electron gun represented an improvement over the basic thermionic emission gun used in the first electron microscopes commercialized by Siemens and RCA.

Development History

The biased electron gun was developed by A. Wehnelt.

Commercialization

The biased electon gun was first commercialized by Siemens.[1]

Note

1. Ralph W. G. Wyckoff, *Electron Microscopy: Techniques and Applications* (New York: Interscience, 1949), 16.

Out-of-Gap Objective Lens

The specimen to be examined by electron microscope must be mounted in, or near, the so-called objective lens of the microscope. An effective design for such a lens will not only have superior electrooptical qualities, it will also have a geometry that allows users to surround the specimen with any needed experimental equipment. The out-of-gap lens performed well on both dimensions. Its unique feature was a geometry that allowed one to place the specimen entirely to one side of the confines of the lens, that is, out-of-gap.

Development History

In 1935 E. F. Burton, who had seen the electron microscope work being done in

Berlin, came to the University of Toronto, Canada, and transferred the idea of an electron microscope to that university. J. Hillier and A. Prebus, working for Burton in Toronto, built successful electron microscopes.[1] Hillier brought the knowledge of that work with him when he became an employee of RCA in 1940. At RCA Hillier built an electron microscope modeled on the design developed by the Toronto group. This design included an out-of-gap objective lens like that used in Toronto.

Commercialization

The out-of-gap objective lens developed in Toronto was commercialized by RCA in their first electron microscope, the RCA Type B of 1941. RCA continued to use this lens design in its commercial microscopes until about 1968.

Note

1. E. F. Burton, J. Hillier, and A. Prebus, "A Report on the Development of the Electron Supermicroscope at Toronto," *Physical Review* 56 (1 December 1939): 1171–72; see also Albert Prebus and James Hillier, "The Construction of a Magnetic Electron Microscope of High Resolving Power," *Canadian Journal of Research* 17A, no. 4 (April 1939): 49–63.

DATA SET FOR SEMICONDUCTOR PROCESS INNOVATIONS

The innovations described in this data set are innovations in the process by which silicon-based semiconductors are manufactured. Most of the innovations are embodied in novel process machinery, but a few are embodied in novel techniques carried out largely by hand.

Selection criteria for this sample will be found in chapter 2. Owing to these criteria, a few important innovations familiar to many readers (e.g., float zone refining) are not represented. In addition, we were unable to find any information on the innovation histories of four innovations included in our sample. These were coded NA in all relevant chapter 2 tables.

Growth of Single Silicon Crystals: The Crystal Puller

Silicon semiconductors—whether individual transistors or integrated circuits—are built up on a wafer sliced from a single crystal of silicon. It is crucial to the performance of the semiconductor that the single silicon crystal used be quite regular in structure and quite free from impurities. The method used for making pure single crystals of silicon for commercial semiconductor manufacture is called crystal pulling. It involves bringing a small seed crystal of silicon into contact with the surface of a bath of molten silicon. Molten silicon in contact with the small crystal is cooled enough to crystallize and thus extend that crystal. Gradual pulling of the seed crystal away from the molten material as crystallization occurs results in a long single crystal rod of pure silicon being grown over a period of time.

Development History

The method of growing single crystals by pulling from a melt dates back to the work of J. Czochralski in 1917.[1] Indeed, the method is sometimes called the Czochralski method. The method was later used by numerous researchers studying single crystals and became well-known in the field.

When Gordon Teal of Bell Laboratories began to study the fabrication of single crystals for use in semiconductors, he decided to adopt the crystal-pulling approach. He and his colleagues first made single crystal germanium by this technique and then began to work on the pulling of silicon single crystals. This proved a very difficult technical task since silicon melts at 1420°C, a temperature at which the containers holding the molten silicon tend to contribute impurities to the melt.

In January 1953 Teal took a job with Texas Instruments, where he formed a materials laboratory. He continued his work on the pulling of single silicon crystals with the aim of producing a commercially usable process. He succeeded, and in June 1954 Texas Instruments used the method in the production of the first commercial silicon transistor.

Commercialization

In the last two weeks of April 1952, Bell Laboratories held a symposium for 34 or so companies who had paid $25,000 each to become licensees of all Bell's proprietary semiconductor knowledge. Central to this information was the technique of crystal pulling. Since the symposium included laboratory visits, demonstrations of equipment, and so on, engineers of licensee companies learned enough to go and build their own crystal pullers. Bell also privately printed a book, *Transistor Technology,* which was distributed to licensees in September 1952.[2] After Bell's 1952 licensing conference, firms interested in manufacturing semiconductors began to build the crystal pullers they needed in-house. Participants in the industry at that time suspected that user firms may have called on outside manufacturers for help in fabricating the equipment to their designs, but they cannot recall the names of any such firms. The first firm we can identify that manufactured the Bell-designed crystal puller as a commercial product was a small firm called Lepel Corporation in Maspeth, New York. According to interviewees at that firm, they built a prototype puller for Bell Laboratories in 1956.

Notes

1. J. Czochralski, "A New Method for the Measurement of the Velocity of Crystallization of the Metals," *Zeitschrift für Physikalische Chemie* 92, no. 2 (1917): 219–21.
2. *Transistor Technology* was privately printed by Bell Laboratories in September 1952. An updated version (with the same title) was published by Van Nostrand, New York, 1957.
3. J. A. Lenard and E. J. Patzner, "A Survey of Crystal-Growing Processes and Equipment," *Semiconductor Products and Solid State Technology* 9, no. 8 (August 1966): 35–42.

Growth of Single Silicon Crystals: Resistance-Heated Crystal Puller

Early crystal pullers for the fabrication of silicon single crystals used radio frequency heaters to melt the silicon being processed. As experience with the process grew, it became clear that resistance heating was both more efficient than radio frequency heating and also more precisely controllable—a very important attribute. As crystal pullers were built that could produce larger diameter crystals, radio frequency heating was increasingly preferred and ultimately became the only type used in production.

Development History

In the mid-1950s it became clear that users preferred the resistance-heated pullers they were building in-house for use in the production of silicon single crystals. National Research Corporation became interested in producing a commercial resistance-heated puller because it was looking for products in which its knowledge of vacuum technology would prove useful. Joseph Wenkus, then an employee of Microwave Associates, a user of crystal pullers, was hired as a technical consultant on the project. Microwave Associates had earlier received a contract from the U.S. Army Electronics Command, Fort Monmouth, New Jersey, to manufacture microwave silicon diodes. As part of fulfilling this contract, Microwave Associates had built a resistance-heated silicon crystal puller about 1953 or 1954. Wenkus transferred the insights he had gained on this project to National Research Corporation, which developed a commercialized version of the equipment.

Commercialization

National Research Corporation introduced its resistance-heated silicon puller in the winter of 1957.

Growth of Single Silicon Crystals: Dislocation-Free Crystal Puller

Imperfections in the lattice structure of single crystals are called dislocations. Any reduction in the number of dislocations in the silicon crystals used to build semiconductors improves the properties of those semiconductors.

Development History

The original work on dislocation-free crystal pulling was done by William C. Dash at General Electric's Schenectady Research Laboratories. General Electric maintained a fairly strong program in materials-purification technology and was a leader in the development of silicon-powered diodes and silicon-controlled rectifiers. The thermal stability and lower resistance of the dislocation-free material was important to the construction of these devices. Dash began his work on dislocation-free growth of crystals about 1956. In April 1959 he published a procedure for the growth of dislocation-free crystals using existing crystal pullers.[1] The essence of the technique was to initially pull the crystal from the melt at a rapid rate that results in a small diameter rod of single crystal. This procedure allows any dislocation existing in the seed crystal to "grow out." After this result has been achieved, the pulling rate is slowed and the rod diameter is allowed to increase to the desired size.

Once Dash published the technique for growing dislocation-free crystals, most semiconductor manufacturers adopted it.

Commercialization

In 1968 Siltec introduced dislocation-free crystal pullers commercially. The hardware difference between these pullers and earlier pullers is relatively small. According to the manufacturer, the dislocation-free pullers required slightly greater standards of cleanliness and temperature control. Appropriate user technique, however, was still required to achieve the desired dislocation-free output.

Note

1. William C. Dash, "Growth of Silicon Crystals Free from Dislocations," *Journal of Applied Physics* 30, no. 4 (April 1959): 459–74.

Growth of Single Silicon Crystals: Automatic Diameter Control

The diameter of the single crystal rod produced by a crystal puller is critically dependent on the rate with which the crystal is pulled from the melt. Since standard diameter rods are needed for further production steps, any oversized rod sections must be ground down and undersized rods must be eliminated before further processing can take place. An automatic diameter control system effectively eliminates either over- or undersized rods, thus eliminating the associated production costs and waste.

Development History

The automatic diameter control system for crystal pullers is essentially an infrared optical system that observes the diameter of the rod being pulled and controls the rate of pull accordingly. Initial work on such systems began at IBM's East Fishkill, New York, facility about 1964 or 1965. The IBM effort was headed up by E. J. Patzner, R. G. Dessauer, and M. R. Poponiak. At that time IBM was in great need of single-crystal silicon for semiconductor production, having just entered into the production of the 360 Series computer. The firm looked to automatic diameter control as one means to increase production capacity.

An initial pilot system using automatic diameter control was in use in 1966. It was turned over to IBM's production department in early 1967. In October 1967, IBM researchers published a very detailed article describing the system and its capabilities.[1]

Commercialization

The first firm to manufacture the automatic diameter control system commercially was Hamco Corporation of Rochester, New York. Hamco introduced it as a feature on the first crystal grower of their manufacture, which they introduced in 1967. Hamco did not license the technique from IBM—they simply adopted it. Other firms did license the system from IBM at a fee that IBM describes as nominal. The first firm to license from IBM was National Research Corporation, which already made crystal growers. Indeed, the original system developed by IBM was built up on an NRC crystal puller.

Note

1. E. J. Patzner, R. G. Dessauer, and M. R. Poponiak, "Automatic Diameter Control of Czochralski Crystals," *Semiconductor Products and Solid State Technology* 10, no.10 (October 1967): 25–30.

Float Zone Crystal Growing

The float zone method of manufacturing single silicon crystals is an alternative to the dislocation-free crystal-pulling technique (which innovation see). It saw little commercial use in the United States but was extensively used in Germany—especially by Siemens. In the float zone technique, a rod of multicrystalline silicon is held in a vertical position by supports attached to both its ends. A small heated ring circles—but does not touch—one portion of the silicon rod. A seed crystal of silicon is next placed against one end of the rod and the heating ring is brought adjacent to it. The heating ring melts the silicon adjacent to the seed crystal. Slow movement of the ring down the length of the rod causes the molten silicon to crystallize into a single crystal following the pattern of the seed crystal. The surface tension of the molten silicon zone keeps the molten material in position in the crystalline silicon rod as the process is carried out.

Development History

Zone refining, a precursor of floating zone crystal growing, was developed by W. G. Pfann, a metallurgist at Bell Laboratories, in 1951. The Pfann process was similar to the floating zone process just described, but it involved placing the material to be crystallized in a crucible rather than suspending it in space. Since molten silicon reacts chemically with most container materials, the Pfann process did not prove usable with silicon. About 1952 H. C. Theurer, also at Bell Laboratories, conceived of the float zone process and reported it in his laboratory diary. Slightly later and independently, Amis and Siemens as well as Paul H. Kech of the U.S. Army Signal Corps developed a similar technique. Kech published his results in 1952.[1] Later, Theurer's diary showed his priority in the invention; eventually Bell Laboratories was assigned a patent.[2]

Commercialization

According to H. C. Theurer, the first firm to commercialize the float zone technique was the German firm of Siemens in the early 1950s. Siemens used the process in the course of manufacturing silicon semiconductors. The first firm to commercially manufacture a float zone process machine was Ecco Corporation, North Bergen, New Jersey, in 1953. Ecco was approached by Paul Kech of the Army Signal Corps, one of the developers of the float zone technique. Ecco was a manufacturer of high-frequency induction heating devices, and Kech placed an order with them for an induction heating device appropriate for the float zone refining of silicon material. After the sale of the initial device ordered by Kech, Ecco modified and enlarged the float zone device, and today it manufactures float zone refining equipment for commercial sale.

Notes

1. Paul H. Kech and Marcel J. E. Golay, "Crystallization of Silicon from a Floating Liquid Zone," *Physical Review* 89, no. 6 (15 March 1953): 1297.
2. U.S. Patent No. 3,060,123.

Wafer Slicing: OD Saw

After a rod of silicon single crystal is manufactured, it must be sliced into very thin circular wafers. The blade thickness of the saw has an important effect on the yield of wafers from a given length of a single crystal rod. Obviously, the thicker the blade, the greater the proportion of single crystal that will be reduced to dust. The so-called OD saw was apparently first used to slice the silicon single crystals used to manufacture semiconductors. The design of the saw is somewhat like a bread slicer with a rotary blade—the outer diameter of which (abbreviated as OD) bears against the single crystal to be sawn.

Development History

Little is known about the development of OD saws. Apparently they were used in a range of industries prior to their application to the semiconductor industry. Who first applied them to the task of slicing semiconductor wafers is not known.

Commercialization

It is not known who was first to commercially manufacture OD saws. Apparently a firm called Do-All was an important supplier of such machines to early semiconductor firm purchasers.

Wafer Slicing: ID Saw

The ID saw has a significantly thinner blade than that used on an OD saw (see preceding entry). The blade of the ID saw is a thin sheet of metal of circular shape with a large circular hole in the middle. This circular blade is clamped around its entire outside circumference, and the edge of the large hole in its center is used as a cutting blade—thus the name ID saw. Material to be sliced is slid into the hole, which is larger than the diameter of a silicon single crystal rod, and then pressed against the cutting edge for slicing.

The rigid clamping of an ID saw blade around its entire outer circumference and the application of some radial tension to the blade makes an ID saw blade much more rigid than an equally thick OD saw blade. Thus ID saw blades of similar performance can be thinner, increasing the number of wafers that can be sliced from a given rod of a silicon single crystal.

Development History

Little is known about the development history of the ID saw. We have learned of, but have been unable to trace, a British patent credited to Sayers that describes the ID slicer. We have also been told of an article in the field of dental research that appeared in a Belgian journal in the mid-1950s. This article reportedly describes an ID saw being used as a tooth slicer.

Commercialization

Capco Corporation, a British company, reportedly sold the first ID slicers used in the semiconductor industry to GE and Raytheon around 1960. In 1961 the Do-All Company apparently licensed the British patent and started production of ID saws. In that same year Hamco of Rochester, New York, began to produce ID saws without a license. Hamco's decision to proceed without a license was apparently based on recollection of the Belgian article, whose publication date preceded the date of the British patent.

Wafer Polishing: Silicon Dioxide Chemical/Mechanical Process

After wafers are sawn from single crystal rods of silicon, their surfaces must be polished. Original practice in the semiconductor industry was to polish these wafers much as glass lenses are polished in the optical industry, that is, with very fine abrasives. Polishing by abrasion was slow and did not leave an entirely damage-free wafer surface on completion. The silicon dioxide chemical/mechanical polishing process cut the polishing time from approximately 1½ hours to approximately 5 minutes. It also resulted in a damage-free surface.

Development History

The silicon dioxide chemical/mechanical process of polishing silicon wafers was developed by R. J. Walsh and A. Herzog of Monsanto Corporation.[1] Monsanto was in the business of supplying polished silicon wafers to the semiconductor industry and Walsh and Herzog were aware of the need for an improved process. The process developed by Walsh and Herzog was not developed theoretically, according to Walsh. When searching for better mechanical abrasives, Walsh experimented with submicron particles of silicon dioxide suspended in an alkaline fluid. The excellent results achieved with this material turned out to be due to chemical as well as mechanical factors—but this result was serendipitous. Monsanto first sold silicon wafers that had been polished by the silicon dioxide chemical/mechanical technique in late 1962.

Commercialization

The silicon dioxide chemical/mechanical process for polishiing silicon wafers can be implemented by using the innovative polishing material in existing polishing machines. According to Monsanto, most suppliers of polished wafers are using the Monsanto technique, but only Western Electric has licensed it from Monsanto. Since no special-purpose machinery is required, no equipment supplier has become involved in the commercialization or dissemination of this innovation.

Note

1. R. J. Walsh and A. Herzog, U.S. Patent No. 3,170,273, issued 23 February 1965, and assigned to Monsanto. Also, Erich Mendel, "Polishing of Silicon," *Semiconductor Products and Solid State Technology* 10, no. 8 (August 1967): 36–37.

Wafer Polishing: Cupric Salt Chemical/Mechanical Process

The cupric salt chemical/mechanical method of polishing silicon wafers was significantly faster than the silicon dioxide chemical/mechanical process used previously (see preceding entry). The process also provides a damage-free mirror surface on silicon wafers.[1]

Development History

The cupric salt chemical/mechanical method of polishing silicon wafers was developed at IBM. IBM manufactures its own semiconductors on a large scale. Researchers were concerned that the technique that IBM was using left imperfect wafer surfaces. Three researchers at IBM had an idea that a solution of water-soluble salts of fluoride and nitride would produce a very slow etching reaction that would improve the quality of the surface. When they tried this solution of salts, they found that the wafers produced were, indeed, perfectly polished. After continued experimentation, however, they found that the valuable polishing action was actually being achieved by cupric ions. These ions were being introduced to the solution inadvertently through corrosion of some of the copper plumbing in the experimental equipment. When this serendipitously discovered effect was understood, they found they could control it well enough for use in commercial production.[2]

Commercialization

IBM began to use cupric salt chemical/mechanical wafer polishing on its in-house production of silicon semiconductor wafers in 1966. It is not clear whether any other firms are using the technique. The innovation was an innovation in polishing solutions only; no change in existing polishing equipment was required.

Notes

1. L. H. Blake and E. Mendel, "Chemical-Mechanical Polishing of Silicon," *Solid State Technology* 13, no. 1 (January 1970): 42–46.
2. G. A. Silvey, J. Regh, and Gardiner, U.S. Patent No. 3,436,259, assigned to

IBM. Also J. Regh and G. A. Silvey, paper presented at Electrochemical Society Meeting, Philadelphia, Penn., 14 October 1966.

Epitaxial Processing: Pancake Reactor

Epitaxy is an important technique used in the fabrication of some semiconductors. The process involves passing a gas containing atoms of silicon or other desired materials over the heated surface of semiconductor wafers. Under proper conditions, atoms contained in the vapor will attach themselves to the surface of the wafer in a manner that continues the crystalline structure of the underlying wafer. The end result is a layer of desired properties that has, in effect, been grown onto the surface of the silicon wafer.

Development History

Researchers at Bell Laboratories had investigated the growing of epitaxial layers on germanium as early as 1950. In 1960 they announced the process as a commercial reality.

Commercialization

Engineers at Western Electric entrusted with setting up a production process for semiconductors containing epitaxial layers began to search for a supplier of the needed equipment—a pancake epitaxial reactor. Ecco Corporation, North Bergen, New Jersey, was conveniently located and capable of performing the work. Ecco was given the design requirements—possibly, but not certainly, including blueprints. Ecco shipped the first commercial epitaxial reactor to Western Electric in September 1961.[1] Sales of Ecco Corporation in 1961 were approximately $1 million.

Note

1. V. Y. Doo and E. O. Ernst, "A Survey of Epitaxial Growth Processes and Equipment," *Semiconductor Products and Solid State Technology* 10, no. 10 (October 1967): 31–39.

Epitaxial Processing: Horizontal Reactor

The horizontal epitaxial reactor performs the same function as the pancake epitaxial reactor (see preceding entry) but is improved in so many respects that it represents a new generation of equipment. Horizontal reactors have an increased wafer capacity relative to pancake reactors and, because of increased automation, yield more uniform results.

Development History

Apparently numerous users experimented with horizontal epitaxial reactor configurations, one of these being Motorola, which in 1961 developed a production horizontal epitaxial system for its own use. Motorola applied this system first to germanium wafers and shortly thereafter to silicon.[1]

According to interviewees at Motorola, much of that firm's technological information related to horizontal epitaxial reactors came from publications that reported some English experimental work. Motorola took out some patents on aspects of their horizontal reactor about 1961. Names reportedly on the patent were T. Law, W. Corrigan, G. Russel, and Klink.

In late 1962 or early 1963 an engineer who had worked on the Motorola project, Larry Jo, left Motorola and began to work at Fairchild Semiconductor. The latter firm was working on an improved horizontal reactor; in 1964 Fairchild did develop both an improved reactor that had larger capacity than earlier reactors and a susceptor made of silicon carbide. (The susceptor is the surface upon which the wafers being treated lie. The wafers can be contaminated by the susceptor if improper materials are used.) Jo found that the Fairchild system was very operator dependent, that is, reproducibility of results was greatly dependent on the individual operating the system. He, therefore, set about developing an automated system.

Commercialization

The first firm to produce the horizontal epitaxial reactor commercially was Semi-Metals, a New Jersey firm in 1965. This firm had not previously been in the business of manufacturing equipment for the semiconductor industry, but was involved in the manufacture of silicon wafers. It occurred to that firm, however, that manufacture of a horizontal epitaxial reactor might be a commercially profitable venture. Larry Jo was hired from Fairchild to be the engineer in charge of the project. According to Jo, the reactor commercialized by Semi-Metals was effectively the same as the one developed by Fairchild in 1964.

Note

1. V. Y. Doo and E. O. Ernst, "A Survey of Epitaxial Growth Processes and Equipment," *Semiconductor Products and Solid State Technology* 10, no. 10 (October 1967): 31–39.

Epitaxial Processing: Barrel Reactor

The barrel epitaxial reactor serves the same function as the original pancake epitaxial reactor (which innovation see). However, it represents an improvement over both the pancake and horizontal reactors in terms of capacity as well as in terms of uniformity of results obtained. The barrel reactor gets its name from its geometry. Silicon wafers to be processed are attached to the outer surface of a cylinder looking somewhat like a barrel. This cylinder is then placed within another concentric cylinder, and the gas used to treat the wafers is passed between the two cylinders while the inner cylinder rotates. The rotation of the inner cylinder insures that all wafers are exposed to the same processing conditions.

Development History

Work on the barrel reactor was begun by IBM in the early 1960s. IBM was driven by a need for higher production capacity for epitaxial wafers. In 1965 the development was presented by IBM researchers at a meeting of the Electrochemical Society.[1] A patent was assigned to IBM in 1969. Apparently several other firms—including RCA, Texas Instruments, and Motorola—replicated the IBM barrel reactor for their own use in the 1960s. It is not clear whether or not these firms licensed the technology from IBM.

Commercialization

In 1971 the barrel epitaxial reactor was commercialized by Applied Materials Technology (AMT), Santa Clara, California. The AMT product utilized the basic configuration of the IBM system. However, it also included an AMT-developed radiant heating system rather than the radio frequency heating system used by IBM. (Wafers are heated as part of epitaxial processing.) AMT claims the use of radiant heat results in a pure and more uniform product and they have patented it.[2]

Applied Materials Technology had sales of less than $16 million in 1971, the year in which it commercialized the barrel reactor.

Notes

1. E. Ernst, D. Hurd, G. Seeley, and P. Olshefski, "High-Capacity Epitaxy Machines," paper presented at Electrochemical Society Meeting, Buffalo, N.Y., 10–14 October 1965.

2. V. Y. Doo and E. O. Ernst, "A Survey of Epitaxial Growth Processes and Equipment," *Semiconductor Products and Solid State Technology* 10, no. 10 (October 1967): 31–39.

Resist Coating: Wafer Spinner

One of the early steps in semiconductor manufacture involves coating of a wafer with a thin film of photoresist—a material formulated to change chemically when exposed to light. This change allows one to selectively remove either the exposed or unexposed portions of the resist film by further chemical processing. It is important to the manufacture of quality semiconductors that the resist coating be put on in a very thin, even layer. Historically, this has been accomplished by placing wafers on a disk, putting a drop of resist on the wafer surface, and then spinning the wafers very rapidly to achieve a thin, even film of resist. The machine that performs these functions is called a wafer spinner.

Development History

It is not clear which user firm was first to develop wafer spinners. It is clear, however, that user firms developed these spinners before commercial equipment producers did. In June 1962 employees then at Fairchild, a major semiconductor maker, report that spinners were in use. These were crude machines—simple aluminum plates with a lip on the outer diameter and a motor underneath. Operators would place several wafers against the lip of the rotor, drip resist on each, and then turn on the motor.

Commercialization

The first commercially produced resist spinner was introduced commercially during or before 1964. Industry participants no longer recall, however, which firm was first to commercialize a spinner. Candidate firms are Micro Tech Manufacturing, Transmask, Preco, and Applied Engineering.

Resist Coating: High Acceleration Wafer Spinner

Wafer spinners are used to spread thin coatings of resist on semiconductor wafer surfaces (see description of basic wafer spinner above). High-speed photography showed that most of the spreading of the resist occurred within the first few revolutions of the spinner and that high acceleration of the spinner could produce a thinner, more uniform coat of resist—both very desirable characteristics.

Development History

The high acceleration spinner was developed by Vern Shipman, an engineer who founded a firm called Head Way Research Corporation, Garland, Texas. Shipman had worked at Collins Radio exploring how to put thin film resist on quartz substrates. He started his firm in June 1964, and in October 1964 decided to build a resist spinner as his first product. At that time he did not have semiconductor manufacturers in mind as customers; instead, he was thinking of electronics firms (e.g., Collins Radio) that needed thin films in order to manufacture other kinds of electronic components. He completed his first machine in December 1964.

Commercialization

Shipman sold his first machine to Texas Instruments in December 1964. From the user's point of view, the high acceleration feature of the Head Way spinner was perhaps most important, but the machine had numerous other useful features as well such as automatic braking on the completion of the resist coating cycle; this increased its productivity.

The high acceleration wafer spinner was the first product of Head Way Research.

Mask Alignment: Split Field Optics

Several masks—each precisely aligned with preceding masks—are required in the fabrication of a typical integrated circuit semiconductor. The mask alignment procedure first used in the industry involved marking two dots at widely different points on a wafer along with two similarly positioned dots on each mask. Operators would then align succeeding masks by visually superimposing the dots on each mask with the dots on the wafer surface.

Early process equipment consisted of a microscope that would allow an operator to focus on one of these dots at a time. The operator would first align a dot on the wafer with a matching dot on the mask as best he could: He would then shift to the other dot and repeat the operation. Since alignment activities on the second dot would disturb the alignment on the first dot, several shiftings back and forth were required before the process was completed. Using this system, skilled operators might be able to align five or six masks per hour.

The introduction of split field optics allowed the operator to see both dots at once and to align both at once. This relatively simple innovation increased the productivity of operators performing mask alignment tenfold.

Development History

Users who developed split field optics and other process innovations typically preferred not to publicize their innovations: They wished to keep knowledge of their success from their competitors. We are thus forced to rely on the recollection of interviewees as to priority in the development of split field optics. According to industry interviewees, Jim Nall at Fairchild was the first to develop a split field alignment system in late 1959 or early 1960.

Commercialization

The first firm to offer split field optic alignment systems commercially was Micro Tech Manufacturing (now a division of Sprague Corporation) in 1963.[1] It is not clear whether Micro Tech developed the split field optics concept itself or whether it acquired it from a user. Ed Forcier, the founder of Micro Tech, was an employee of Fairchild at the time that Nall developed the split field system there. Thus, he might have been in a position to learn of it at Fairchild. On the other hand, Ed Jasiewicz, general manager of Micro Tech in 1974, felt that the system was developed entirely in-house.

In 1964 Kulicke and Soffa (K&S) also announced a split field mask alignment system. The genesis of their product was, they report, an approach by a representative of Nikon, the Japanese optical firm, who offered to sell them a set of split field optics usable in a split field optics mask alignment system.

Note

1. Micro Tech Manufacturing, Advertisement, *Semiconductor Products* 6, no. 8 (August 1963): 62.

Mask Alignment: Automated System

An automated mask alignment system automatically performs the alignment work previously performed by an operator using a split field optical system (see preceding entry). The principal advantage of the system is increased speed and increased accuracy—the latter improves the yield of finished semiconductors of good quality.

Development History

The key firm in the development of automated mask alignment systems was Computervision of Medford, Massachusetts. This firm is an equipment manufacturing firm; according to industry interviewees, no user development work preceded their efforts.

Computervision was formed in the late 1960s by three engineers, one from Singer Corporation and two from Concord Controls Corporation. Their goal was to produce automated devices. One of their initial products was an automated mask alignment system. According to Michael Cronin of Computervision, the company founders were told by most manufacturers that it was impossible to build an automated alignment system and that IBM had apparently tried with no success to fabricate one. Computervision initially tried to induce Kulicke and Soffa, a firm well-known for optical alignment systems, to engage in a joint venture. When Kulicke and Soffa expressed no interest, Computervision bought one of the standard K&S systems, modified it for automatic operation, and then showed it to Kulicke and Soffa. At last, K&S was sufficiently impressed with it to enter into a joint venture for the production of the device.

Commercialization

The first models of the K&S/Computervision auto aligners were offered at the WESCOM show in 1970. About 50 of the systems were sold, but they had problems that, a year or two later, led K&S to discontinue its involvement with auto aligners and with Computervision. Computervision then acquired Cobilt Corporation in California, a small concern producing manual aligners, and in 1972 introduced a new series of auto aligners, which became the first fully successful commercial product in the field.

Silicon Junction Fabrication: Diffused Junction Furnace

Silicon transistors are made up of regions "doped" with *p*-type and *n*-type impurities. Where these regions meet, a so-called junction is formed. Such junctions are the real operating heart of semiconductor devices.

The first silicon transistors sold commercially had so-called grown junctions. Grown junction technology appears to have been developed independently at Bell Laboratories and at General Electric. At Bell Labs the initial work was carried on by Morgan Sparks and Gordon Teal, with the first publication regarding the process appearing in 1951.[1] Work at GE on grown junctions was carried out by R. N. Hall and his associates. Grown junctions are created by simply adding impurities of the proper type to a silicon crystal as it is being grown. For example, if one begins to grow a crystal from molten silicon containing a *p*-type impurity, then the resulting crystal will be *p*-type. Addition of sufficient *n*-type impurity to overwhelm the *p*-type impurity during the growing process of this crystal will result in a switch from *p*-type to *n*-type silicon—with the point at which the transition takes place being a grown junction.

The dominant method used to produce silicon junctions today is called the diffusion method. This method was developed at Bell Laboratories, which called a second symposium of its licensees to inform them of the technology in 1956. This process involves heating silicon wafers in a furnace to a precise temperature for a precise time, and at the same time passing a gas containing the desired *p*- or *n*-type material that one wants to use to form a junction through the furnace. The high temperature in the furnace allows atoms of the impurity to diffuse into the crystal structure of the silicon to a known concentration and a known depth, thus creating a diffused junction. The process equipment used to create diffused junctions is called a diffusion furnace. It is essentially a furnace in which the temperature and the introduction of the impurities can be controlled very precisely.

Development History

The first diffusion furnaces used to manufacture diffused junction transistors commercially were built by user firms. Later, manufacturers of laboratory furnaces custom-built furnaces to user specifications.

It took several years for the furnace users to fully understand what the critical parameters of the diffusion process were. When it became apparent that the temperature stability and control were extremely critical to the production of good diffused junction semiconductors, furnace manufacturers were able to respond very quickly with precisely controllable furnaces.

Commercialization

In 1961 the Heavy Duty Electric Division of Sola Basic Products Company introduced a line of special-purpose diffusion furnaces at the WESCOM show.

Note

1. W. Shockley, M. Sparks, and G. K. Teal, "*p-n* Junction Transistors," *Physical Review* 83, no. 1 (1 July 1951): 151–62.

Silicon Junction Fabrication: Ion Implantation Accelerator

Silicon junctions in semiconductors are created by bringing *n*-type material into close contact with *p*-type material. This is done by introducing *n*-type impurities into a region of a *p*-type material, or vice versa. Ion implantation—a method of introducing such impurities—has the potential of being more precise than the thermal diffusion method (see preceding entry). The method involves first ionizing atoms of the desired impurity and then accelerating them to a known speed by means of an ion accelerator. The ion beam thus created is aimed at specified points on the silicon wafer surface, and the ions penetrate into that surface to a precisely known depth and concentration.

Development History

Some early experimental work on ion implantation was performed at Bell Laboratories in the early 1950s.[1] The commercial success of the diffusion process, however, delayed serious commercial interest in the ion implantation technique until the 1960s. In the early 1960s a significant amount of experimentation with ion implantation was conducted by Hughes Laboratory at Newport Beach, California (H. G. Dill and R. W. Bowers were among the principal investigators); by Bell Laboratories at Murray Hill (A. McRae was a principal investigator); at AFCRL (Dr. Rooslid was a principal investigator); and at an Ion Physics joint venture with Signetics Corporation. The Ion Physics/Signetics group apparently did produce some ion-implanted devices for the U.S. Air Force in the early 1960s, and they published a discussion of methods for producing such devices in 1965.

Commercialization

Early experimental work on ion implantation was conducted using laboratory-type ion accelerators that were commercially available from several sources. Ion accelerators specifically designed to be used in the production of semiconductors were probably first commercialized by High Voltage Engineering in about 1969.

High Voltage Engineering was a partner in a venture to develop ion-implanted devices called Ion Physics/Signetics. In its work it did develop ion implantation accelerators, but it was prevented by its partnership agreement from selling these commercially—the venture was interested in selling devices only. When the Ion Physics/Signetics venture was dissolved in 1968 or 1969, High Voltage Engineering was free to pursue the sale of ion implantation accelerators. It sold only a few of these, however, before deciding that the field was commercially unattractive.

The second firm to commercialize an ion implantation accelerator specifically designed for semiconductor implantation work was Accelerators, Inc. Hughes had bought 20% of Accelerators stock in 1968 or 1969, and Hughes scientists designed the production-oriented accelerator sold by them. In 1970 Accelerators shipped their first production-oriented accelerator to Hughes at Newport Beach. Previously, Accelerators, Inc., had produced laboratory-type accelerators.

In 1971 Extrion Corporation began to produce production-oriented ion accelerators. Extrion was a start-up company formed by employees of High Voltage Engineering who left that firm when it decided to stop producing accelerators for semiconductor ion implantation work.

Note

1. W. Shockley, U.S. Patent No. 2,787,564, issued in 1954.

Scribing and Dicing: Automated Mechanical Device

In the process of making semiconductors, many circuits are fabricated simultaneously on a single wafer of silicon crystal. When completed, these circuits must be physically separated from each other, and this is done by breaking the silicon wafer on which they were fabricated into tiny square chips—each containing only one circuit.

In the earliest days of the industry, the scribing-and-dicing process step was carried out by a worker who, with the aid of jigs and fixtures, scratched lines manually between the circuits on a wafer with a sharp diamond point and then broke the wafer along those lines with the aid of a straightedge. This manual process was slow and subject to worker error. For example, a worker might easily tire and scribe a line through the middle of some circuits instead of along their edges—and thus ruin them. To improve yield and to lower costs, automatic machinery was developed to perform the scribing-and-dicing task. The initial generation of such equipment simply automated the process previously carried out manually. That is, a diamond point was mounted on a machine that would move the point in such a way as to scribe the wafers at the proper locations.

Development History

Several semiconductor manufacturing firms may have developed their own automatic scribing-and-dicing machines. The device with the closest link to the first autoscriber produced commercially was that built by Western Electric engineers at their Allentown, Pennsylvania, plant. Western began using their internally developed autoscribers in 1958 or 1959.

Commercialization

The first automatic scribing-and-dicing machine to be placed in the commercial marketplace was introduced by Kulicke and Soffa in March 1960. K&S was formed in the early 1950s as a machine design firm. In 1958 they observed the automatic scriber and dicer developed by Western Electric when they were invited into a Western Electric plant to perform an unrelated machine design task. K&S felt that there might be a commercial market for such a machine and proceeded to design a commercial version.

In 1965 Tempress also introduced a commercial automatic scribing-and-dicing machine. Tempress was formed by former Fairchild employees and, according to interviewees at that firm, the Tempress product embodied scribing-and-dicing technology developed at Fairchild.

Scribing and Dicing: Laser Scriber and Dicer

Laser scribing-and-dicing equipment performs precisely the same function in the semiconductor fabrication process as does the earlier mechanical scriber and dicer (see preceding entry). Its main difference is that it substitutes a laser beam for the diamond cutting tool used in the mechanical scribing-and-dicing machine. The laser beam offers the user two major advantages over the earlier diamond scribing machine. First, it is much faster. Second, the laser beam cuts much more deeply into the wafer than did the diamond cutting tool. These deep cuts make the process of separating the wafer into individual chips more accurate and thus increase yield.

Development History

Quantronics of Long Island, New York, was a manufacturer of lasers. In 1968 it was actively involved in trying to find applications for these. During a trip to Texas Instruments, a semiconductor manufacturer, Quantronics discovered that the firm had tried unsuccessfully to build a laser scriber system. They tried to persuade Texas Instruments that Quantronics could succeed where Texas Instruments had failed and that the latter should join them in a joint venture. Texas Instruments was not interested, however. Later in 1968, Quantronics was able to interest Motorola in a laser scribing system.

In 1968 Quantronics and Motorola entered into an informal joint effort in which Motorola supplied Quantronics with some development funds and a great deal of technical information on the desired characteristics of a laser scribing system.

Commercialization

Quantronics offered a laser scriber and dicer commercially in 1970. The first unit was shipped to Motorola. Immediately thereafter Texas Instruments purchased 24 units at $70,000 per unit.

In about 1971 Electroglas also commercialized a laser scribing-and-dicing machine. In the 1970s Quantronics and Electroglas held the major share of the market for laser scribing-and-dicing machinery.

Wire Bonding: Thermocompression Bonding

Semiconductor chips must be linked electrically to the outside world in order to function. This electrical linking is achieved by means of tiny metal wires that are physically bonded to the semiconductor chip on one end and to an electrical connector on the other. The bonding of the wire to the surface of a semiconductor chip is a difficult task. The wire must make a good electrical connection that will not degrade with time.

The earliest means of bonding wires to commercially produced silicon semiconductor devices involved tiny balls of solder that in essence soldered the wire to the chip. These solder bonds proved difficult to produce reliably. Sometimes the joint was mechanically weak; at others the solder joints would form a diode junction with the semiconductor materials and thus degrade the performance of the semiconductor.

Thermocompression bonding, the innovation under consideration, involves heating the semiconductor surface to about 200°–300°C and then simply pressing the wire to be bonded against the semiconductor chip surface at the appropriate place with a pressure from 5000 to 10,000 lb/sq in. In a few seconds a bond with excellent physical and electrical properties is formed. The machine that performs this task is called a thermocompression bonder.

Development History

Thermocompression bonding was developed by three scientists of Bell Laboratories: O. L. Anderson, H. Christensen, and P. Andreatch. Most of the work of this team was performed in the 1955–58 time period. The team published its findings,[1] and the need was so great that many semiconductor manufacturers built their own thermocompression bonders in-house in the 1957–59 period.

Commercialization

The first commercial thermocompression bonder was offered by Kulicke and Soffa in late 1959. Demand for the product was so strong that within a year of introduction, net sales exceeded $1 million.

K&S observed thermocompression bonding in production equipment that was operating at a Western Electric semiconductor plant in 1958. K&S engineers made only minor mechanical modifications to the Western Electric thermocompression bonder before commercializing it.

Note

1. O. L. Anderson, H. Christensen, and P. Andreatch, "Technique for Connecting Electrical Leads to Semiconductors," *Journal of Applied Physics* 28, no. 8 (August 1957): 923.

Wire Bonding: Ultrasonic Bonding

The ultrasonic bonding of metals involves rubbing together the two pieces of metal to be bonded with such high energy that surface impurities on the two metal surfaces to be bonded are scrubbed away and the underlying atoms of metal brought into close enough contact to form a good bond. In ultrasonic bonding, the energy for mechanically rubbing the two pieces of metal together is provided by a tool that vibrates mechanically at an ultrasonic frequency.

Development History

Ultrasonic bonding as a general welding technique was discovered in the 1950s. Its first application to the attachment of wires to semiconductor chips apparently occurred in the mid-1960s, according to interviewees at Sonobond Corporation, Westchester, Pennsylvania, a supplier of ultrasonic welding equipment. Who was actually first to develop an ultrasonic bonder for semiconductor manufacturing use is not clear. It appears that Sonobond initially supplied ultrasonic transducers—the generators of ultrasonic energy needed for welding—to Fairchild and Motorola who then designed the first ultrasonic bonding equipment in-house.

Commercialization

Ultrasonic bonding equipment for the bonding of wires to semiconductor chips was commercialized by Sonobond in the 1960s. The corporation initially provided only the source of ultrasonic energy to semiconductor manufacturers but later commercialized a complete machine for the ultrasonic bonding of wires to semiconductor chips.

Mask Graphics: Optical Pattern Generator

The patterns of light and shadow that expose the resist-coated semiconductor wafers are generated by so-called masks. These masks must be very precise, and their creation is a demanding task. They are created on a large scale—perhaps 5 ft by 5 ft—and then photographically reduced. Masks were first created by a hand technique much like drafting: A desired pattern was cut out of a material called Rubylith by means of a straightedge and a small hand-held knife. When integrated circuits became more complex, the patterns needed in masks became more complex, and it was no longer practical to produce these masks by hand. The solution to the problem was a numerically controlled machine that exposed a large sheet of photographic material in the desired pattern.

Development History

Interest in automated mask generation began in the mid-1960s with the realization that large-scale integration required masks too complex to be cut manually. Bell Laboratories and IBM were among the first to attempt to create automated mask generation machines. Their initial attempts involved computer-driven knives that basically automated the former handwork of cutting a Rubylith pattern.[1] This technique was eventually found unpromising: Even though the Rubylith material was automatically cut, human operators still had to select which sections of material were to be stripped away from the pattern and which left behind. Mistakes made in this process were as devastating as mistakes made in the cutting process.

The innovation developed at IBM and elsewhere involved mounting a large photographic plate on a table that could be moved in the *x* and *y* directions under numerical control. A photographic projector would then project various-sized rectangles as specified by a computer program in order to create the pattern of light and shadow specified for a particular mask design.[2]

Commercialization

In July 1967 R. C. Beeh, an employee of OPTO Mechanisms, described a device that appeared to be a commercial automated pattern generator.[3] OPTO Mechanisms is, however, no longer in business and, although the product pictured in Beeh's article appears to be a commercial device, it is not clear that one was ever sold. (According to industry interviewees, OPTO Mechanisms did receive an order for one unit from Texas Instruments. That unit was never accepted by Texas Instruments, however, which apparently contributed to OPTO Mechanisms' eventual bankruptcy in about 1971.)

The first automated optical generator for the manufacture of semiconductor masks that was produced by an equipment manufacturer and successfully sold was put on the market in April 1968 by GCA/David W. Mann Company. The Mann system was much like the IBM system described in July 1967. The machine involved a numerically controlled pair of perpendicularly mounted slits. A light was mounted behind the slits and, depending on the position of the slits, was projected on a photographic plate mounted on an *x-y* table as a rectangle of any desired dimension. A suitable choice of rectangles and suitable positionings of the *x-y* table could be combined to build up any desired mask pattern.

Since its introduction in 1968, the original model 1600 optical pattern generator has been steadily improved. By 1976, a model was available that was about 10 times faster than the original model.

Notes

1. See H. O. Hook, "Automated Mask Production for Semiconductor Technology," *Semiconductor Products and Solid State Technology* 10, no.7 (July 1967): 35–38; and P. Donald Payne, "Photomask Technology in Integrated Circuits," *Semiconductor Products and Solid State Technology* 10, no.7 (July 1967): 39–42.
2. See note 1.
3. Roland C. M. Beeh, "A High Accuracy Automated Microflash Camera," *Semiconductor Products and Solid State Technology* 10, no.7 (July 1967): 43–49.

Mask Graphics: Electron Beam Pattern Generator

The major advantage electron beam mask pattern generation devices provide relative to optical pattern generators is their higher resolution: Optical systems are limited to about 7 Å spot size, whereas electron beam systems can produce a ½ Å spot size. The higher resolution obtainable with electron beam devices in turn allows users of the systems to make more complex and denser masks for integrated circuits.

Development History

The early history of electron beam pattern generators is difficult for us to discover because a great deal of the early work was apparently done outside the United States. The earliest advertisement we can find for a commercialized electron beam device appears in *Solid State Technology* in 1968: It describes a computer-controlled masked generator of the electron beam type offered for sale by JEOL, a Japanese corporation. The first work in the United States on an electron beam mask generator was apparently begun in 1966. In that year research was begun at a Bell Laboratories research center in Princeton, New Jersey, that resulted in the creation of experimental devices during the next three or four years. In 1971 Bell Laboratories used a system of its own design to manufacture actual integrated circuit masks at its Murray Hill facility.

Commercialization

The first electron beam mask pattern generator offered for commercial sale in the United States was apparently that advertised by JEOL in 1968. The development history of that system and its eventual commercial success or failure are not known to us.

Mask Reduction: Two-Stage Step and Repeat Reduction Process

A two-step process is used to reduce the black-and-white pattern for an integrated circuit mask from its original size of perhaps several feet square to the miniature size necessary for actual use in connection with producing tiny integrated circuits. The process consists first of reducing the full-size layout by a factor of perhaps 20 by means of a precision camera. A second precision camera then reduces the image by another factor of 20 or so and then "steps" the reduced image across a photographic plate, thus creating multiple images of the same mask pattern. This plate is then used to produce multiple integrated circuits on a single wafer of silicon.

Development History

The two-stage step and repeat mask reduction process was developed almost simultaneously by two user groups and by a manufacturer of equipment—all apparently working independently. The first work was done by users at Fairchild Semiconductor about 1959. Gordon Moore of Fairchild recalls that Bob Noyce constructed a two-step photo-reduction system for internal use at Fairchild about 1959. Fairchild, however, made no attempt to commercialize this device; indeed, it strove earnestly to keep it secret.

From 1959 through 1961 researchers at Diamond Ordnance Fuze Laboratories, located in Washington, D.C., also developed a two-step mask reduction process. T. C. Hellmers, Jr., and J. R. Wall reported their work in detail in a January 1961 article.[1] About 1960 GCA/David W. Mann Company began to develop a two-stage step and repeat mask reduction machine for commercial sale. That firm had been receiving orders for masks from semiconductor firms (the first such firm being Transitron) since early 1960. Since GCA/David W. Mann was essentially an instrument-manufacturing company, not a service-providing company, their thoughts naturally turned to manufacturing a device rather than providing a service.

Commercialization

GCA/David W. Mann was the first firm to make a two-stage step and repeat mask reduction device available to semiconductor manufacturers commercially. They first showed the device in the spring of 1961 and sold the first one to Clevite Corporation on 28 April 1961.

GCA/David W. Mann had sales of under $2 million in 1961. Fairchild Semiconductor had sales of approximately $43 million in 1959.

Note

1. T. C. Hellmers, Jr., and J. R. Nall, "Microphotographs for Electronics," *Semiconductor Products* 4, no. 1 (January 1961): 37–42.

DATA SET FOR PULTRUSION PROCESS MACHINERY INNOVATIONS

The innovations described in this data set are associated with pultrusion process machinery. The innovation history of the pultrusion process is followed from the original rudimentary equipment through the major process machinery improvements that have been commercialized over the years. Sample selection criteria are discussed in chapter 3.

Because the manufacturers and users of pultrusion equipment do not often document their innovations in publications, most of the information comes from interviews held with employees of pultrusion equipment manufacturer and user firms who had direct knowledge regarding the sampled innovations.

Original Batch Pultrusion Process

Pultrusion machines fabricate fiber-reinforced plastics products of constant cross-section. An everyday example of a pultruded product is the fiberglass-reinforced rod used by the makers of fiberglass fishing rods. In essence, pultrusion machines create pultruded products by quite a simple process. Reinforcing material such as fiberglass roving or cloth is first wetted with a thermoset resin such as polyester, then pulled through a heated block of steel (a die) that has a hole in the middle of a cross-section matching that of the desired pultruded product. When the wetted reinforcement has been drawn completely through the die, the resin has cured around and between the strands of reinforcing material, and the reinforced plastic product—a pultrusion—is complete.

Reinforced plastic product made by means of the pultrusion process is characterized by a very high percentage of reinforcing material that is aligned in known directions. (In contrast, ordinary reinforced plastic is characterized by short lengths of reinforcement fiber oriented randomly within the plastic matrix.) These characteristics make pultrusion especially appropriate for applications in which high stress is applied to the part in directions parallel to the embedded material.

Development History

The first pultruded products were long, thin fiberglass-reinforced cylinders used in the manufacture of fiberglass fishing rods. These were manufactured by Ocean City Manufacturing Company, Philadelphia, starting approximately in 1947. The pultrusion process developed by this firm was a simple batch process that involved hand tooling. Fiberglass rovings (a threadlike form of fiberglass reinforcement) were collected by hand into bundles about the thickness and length of a fiberglass fishing rod blank. These bundles were dipped into a container of room-temperature-cure polyester resin and then passed through a steel plate with a hole in it the size of the diameter of the rod being produced. This primitive die served to squeeze the rovings tightly together and eliminate excess resin. The resulting bundle was then hung from a hook until it cured.

Commercialization

The simple tooling required by this early pultrusion process was never produced commercially by a machinery builder. Today, this process is obsolete.

Intermittent Pultrusion Process

The first pultrusion process simply pulled a bundle of resin-wetted reinforcement through a die to shape it; it then would require several more hours to fully cure. If one could cure the pultrusion fully while it was still inside the die, one would have much more rapid processing times as well as more precisely dimensioned pultruded parts. The innovation described here was designed to obtain these advantages. Instead of simply being pulled through a thin plate for shaping as in previous practice, wetted roving was pulled into a tubular die several feet in length. Because this die was heated, the length of material within it was fully cured in a matter of minutes. After curing, pull was resumed on the now-cured section of pultrusion in the same direction as before. This pull drew the cured section out of the die and at the same time drew a new uncured wetted roving into the die behind it. When the die was once again fully filled with uncured material, pulling would stop and the curing cycle would begin again. A crucial (patented) invention that made the process possible involved placing a cooled section at the front of the heated die just described. This prevented resin from curing before it was pulled inside the die and formed to proper dimension.

Development History

The intermittent pultrusion process was developed by Roger White, president of Glastic Corporation, Cleveland, Ohio, in 1948. White had received a large order for a part of constant cross-section (spacer sticks for motor armature windings). As White recalls, attempts to fabricate the parts by conventional sawing and machining operations proved too expensive, thus inducing him to develop the new method.

Glastic Corporation was a small firm and did not have an established R & D budget. White estimates that he spent perhaps $5000 in direct costs to develop the intermittent pultrusion process.

Commercialization

White used the intermittent pultrusion process commercially within the Glastic Corporation from about 1950 to 1966. He tried to keep the process proprietary because it was significantly cheaper than alternative ways of making motor armature spacer sticks and allowed him to make a 30% or 40% profit on his sales of approximately $100,000 per year for the years 1951 through 1956. In 1956 a competitor hired away one of White's engineers and induced him to replicate White's proprietary process. As a consequence, profits for spacer sticks fell. White sued in an attempt to enforce his patent and after the expenditure of much time and money was awarded only $15,000 by the court, which also allowed the competitor to continue his infringement.

It appears that White's process machinery innovation was never used beyond the two firms discussed here. By the 1960s the continuous pultrusion process using a heated die (which innovation see) had advanced so far that Glastic discontinued the use of the process described here.

Tunnel Oven Cure

Some pultrusions need not be finished to a high tolerance (e.g., fishing rod blanks are machined after being pultruded; thus tolerances in the pultruded part are not critical). For such applications it would be advantageous to achieve the rapid processing rates characteristic of heat-cure pultrusion without the constraints of a heated die. Tunnel oven curing meets these requirements. In this process, fiberglass roving is wetted with resin, shaped, and then pulled through a tunnel oven—a long heated chamber in which the shaped roving and resin bundle is cured by radiant energy from the chamber walls rather than by contact with the heated die surface.

Development History

The tunnel oven cure/continuous pull pultrusion process was developed by Sam Shobert, president of the Polygon Corporation, Walkerton, Indiana, in 1950. At that time Shobert was involved in the manufacture of fishing rod blanks, using a slow, labor-intensive molding technique. Large customer orders prompted him to search for a faster method for making the product. Shobert estimates that the direct cost of the development project was less than $10,000 for materials, plus labor.

Commercialization

The tunnel oven cure/continuous pull pultrusion process worked well. Shobert's firm made hundreds of thousands of fishing rod blanks, and Shobert estimates that at "one time" they had about 80% of the market. Their profit on these was not high, however, ranging from 3% to 7% pretax. General Electric expressed some interest in using the process to make winding pins—a component of electric motors. Polygon gave them a license and built them two machines for a total price of approximately $50,000. Two years later, GE asked Polygon to take back the machines and produce the part for them, finding this a more economical arrangement. Polygon agreed, and produced $750,000 to $1,000,000 of the parts for GE for many years at a pretax profit of 20%.

In recent years Polygon discontinued the tunnel oven process in favor of standard pultrusion, using a heated steel die, which had improved over the years and had become a more economical alternative.

Heated Die Cure/Continuous Pultrusion Process

Prior to the die cure/continuous pultrusion innovation, pultrusions cured within a heated steel die could not be moved while curing. This was because polyester resin, the thermoset resin universally used in the early days of the pultrusion process, turned into an excellent adhesive when partially cured, gripping the die tightly at that point. Later, when fully cured, this stickiness disappeared and the completed pultrusion could be slid from the die. It was found that the mixing of lubricants such as carnuba wax into polyester prior to curing would prevent the partially cured polyester from sticking to the die surface. With this discovery, it became possible to create pultrusion process machines that steadily and continuously drew material through the die during the curing process.

Development History

The discovery of the value of internal lubricants in the pultrusion process and the development of the first truly continuous pultrusion process machine were achievements of Roy Boggs, an employee of Universal Molded Products Corporation in 1955 (today known as Morrison Molded Fiberglass Company, Bristol, Virginia). In 1955 Morrison Molded Fiberglass had obtained a large order for fiberglass handrails from the Federal Aviation Administration, and Boggs decided to experiment with new methods for producing these. No formal R & D budget was involved. He simply put equipment together out of material available on the shop floor. After numerous failures caused by partially cured polyester resin adhering to the inside of his steel dies, Boggs hit on the key idea of embodying lubrication in the resin itself. When he got the process to the point where it would run a few feet without jamming, he showed it to his management, which encouraged him to patent. Eventually Boggs obtained and assigned to Universal Molded Products more than 30 patents on the pultrusion process.

Commercialization

Universal Molded Products quickly became the largest manufacturer of pultruded products in the world. Its successor firm, Morrison Molded Fiberglass, retains this distinction today, having an estimated 20% market share.

Morrison Molded Fiberglass has not licensed its patents to U.S. competitors nor attempted to enforce its patent rights to the pultrusion process in the United States. It did not have a really basic patent and perhaps felt it could not prevail in U.S. courts. On the other hand, in 1960 it did begin an active program of licensing foreigners to use the pultrusion process and did and does build machines for foreign licensees. Foreign licenseees who buy pultrusion machines from Morrison pay an initial royalty fee of $40,000; then, they are subject to a contract that provides for continuing royalties. (When and if foreign licensees refuse to honor these contracts—as many have—Morrison does not attempt to enforce its rights legally, suspecting that likelihood of success would be slim.) Morrison's annual fees from foreign licensees from 1960 to present was not more than $100,000 per year. Morrison currently has 13 licensees.

The continuous pultrusion process reduced labor content from 50%/60% to 5%/10% of the product direct cost relative to the hand layup process it superceded. It is the basis of all current pultrusion processes.

Tractor Pullers

Initial continuous-pull pultruders supplied the mechanical force needed to pull the material through the process either by winches or by so-called nip roll pullers. Nip roll pullers consisted simply of powered wheels squeezing the pultrusion between them and pulling it along—much as the opposed rollers of an old-style washing machine laundry ringer drew material between them. Both systems had major drawbacks, however. Winches were obviously not suitable for providing continuous pull over a long span, and it was quickly found that nip roll pullers could not exert sufficient force. The traction required to pull pultrusions through a system was found to be as much as 200 lb/in. of perimeter of the pultrusion. To meet this problem, so-called tractor pullers were designed. These looked much like the treads of two bulldozers put face to face. They supplied greatly increased pulling power.

Development History

The first tractor puller used in pultrusion was designed by Roy Boggs of Universal Molded Products (currently Morrison Molded Fiberglass, Bristol, Virginia). The design task was found to be relatively difficult: Too much pressure and the pultrusion would be crushed; too little, and the tractor pullers would slip ineffectively. Boggs recalls that it took $20,000 in direct cost to build the first pullers capable of pulling pultrusions with a 14-in. perimeter.

Commercialization

The ineffectiveness of nip roll pullers for pultruding products with perimeters larger than 1 in.-or-so was glaringly apparent to all users of pultrusion process machinery. All these firms quickly turned to tractor pullers and made these standard industry practice. Since building pullers was relatively complex, and since Morrison—the innovator—would not build them for U.S. competitors, many users searched for outside suppliers. The firm that eventually emerged as a major producer of this component of pultrusion machines is the Gatto Corporation. This firm had earlier been in the business of tractor pullers for less demanding applications. When pultruders informed them of the new application, they proceeded to develop an appropriate puller. Gatto estimates that it cost them perhaps $50,000 to $100,000 to develop the new product.

Cut-off Saw

As the pultrusion process became more rapid and reliable, it became important to have some means of automatically cutting the continuously emerging pultrusion into the lengths required by customers. An automatically activated saw called a cut-off saw filled this need.

Development History

Automatic cut-off saws were used in numerous other industries for sectioning continuously produced products. It therefore seemed logical to apply this device to a similar task in the pultrusion industry. The adaptation, although very useful, seemed so unremarkable to participants in the industry that it is not clear to them who in fact was first to do so. Probably several users brought this innovation to the pultrusion industry independently.

Commercialization

The use of cut-off saws is universal in the pultrusion industry today. Since cut-off saws did not have to be specially adapted to the requirements of the pultrusion industry, no special source of saws can be pointed to. At the time cut-off saws were adapted to the pultrusion process, the price of such a saw was approximately $1500. Interviewees estimate it would have cost perhaps $500 to install the saw on a pultruder.

Augmented Radio Frequency Cure

Preheating of thick-walled pultrusions with radio frequency energy before they enter a standard steel die is the essence of the radio frequency augmented cure technique. It very effectively serves the purpose of accelerating the rate at which such products can be cured because heated steel dies can only heat a product from the perimeter, and it takes a long time for heat to penetrate to the center of a thick section. In contrast, radio frequency energy heats the entire product at once.

Development History

Radio frequency augmented cure was developed by Brant Goldsworthy in 1968. The innovation is simply implemented by placing a radio frequency heating unit ahead of the die location on an otherwise standard pultruder. At the time of the innovation, Goldsworthy owned both a pultrusion process machine user company, Glastrusions, Inc., and a commercial manufacturer of pultrusion equipment, Goldworthy Engineering.

Commercialization

From 1968 to 1977 Goldsworthy sold perhaps a dozen radio frequency augmented cure systems. It was his practice to sell them as accessories, with a list price of approximately $25,000 for the commercial pultruders sold by Goldsworthy Engineering. No other firm has undertaken to supply such units to pultruders.

Preforming Tooling

As the size of pultruded products increased and as their shapes became more complex, it was no longer sufficient to simply pull the various strands of reinforcement material making up a pultrusion into the die. Instead, accurate placement of the various strands of roving and strips of reinforcement mat (a form of cloth made of reinforcement) became necessary. The range of racks and hooks and other specially designed tooling that performs this guidance function is called preforming tooling.

Development History

Preforming tooling is very much like software on computers in the sense that it must be designed anew for each specific application. Thus, every user who must pultrude a new product—or pultrude an old product on a new machine—is forced to design preforming tooling. The use of preforming tooling is now universal in the industry, except for the simplest shapes.

Commercialization

There are no commercial manufacturers of preforming tooling. All users devise their own as part of their product-engineering task.

Hollow Product Tooling

The development of hollow products—especially those with hoop strength—required tooling more complex than that required in the fabrication of solid products. Various solutions were developed, including apparatus for braiding and apparatus for winding strands of material in a hooplike fashion around the strands of reinforcement material being pulled through the process machinery.

Development History

Any of three pioneering pultrusion user firms may have been the first to develop hollow product tooling. Each used a somewhat different approach. Goldsworthy of Glastrusions used an overwinder approach; Shobert of Polygon used a braiding approach; and Boggs of Universal Molded products developed a very elaborate special-purpose approach. (Universal Molded Products had a massive order for 5-in. rocket tubes from the U.S. Army Chemical Corps. Approximately $700,000 was expended to tool up for this particular hollow product.)

Commercialization

There still is no standard approach in the field to manufacturing hollow products. User firms build their own hollow product tooling for each product at a cost typically ranging from a few hundred to a few thousand dollars.

Improved Dies

Dies are built with a hole through the center that has the shape of the cross-section of a pultrusion being produced. For this reason a new die has to be manufactured for each new product one wishes to pultrude. Over the years, dies have been improved in several ways. They have been made smoother; they have been heated in a more precisely controlled manner; and their geometry has been improved. The result of these incremental improvements has been twofold: (1) the amount of scrapped product has been reduced down to approximately 5% from an initial rate several times higher and (2) the speed of the pultrusion process has been increased.

Development History

As noted above, dies are built anew for each product to be pultruded. Typically, they cost a few thousand dollars to build and their cost is charged to the customer as a set-up or tooling charge. The incremental improvements that have been applied to dies over the years are not the product of a separate R & D effort. Instead, lessons learned from previous die performance cause designers to modify new dies slightly. Modifications that result in improved performance are noted and become part of a firm's process know-how.

Commercialization

Owing to the special-purpose design of each pultrusion die, no firm manufactures them as a standard, commercial product. Dies are either built by user firms themselves or by tool and die firms to the specifications of user firms.

DATA SET FOR THE TRACTOR SHOVEL

The data set for the tractor shovel documents the development of the wheeled tractor shovel in 1939 and the 10 major innovations that significantly improved it over the succeeding 20 years. Sample selection criteria are found in chapter 3.

Because manufacturers and users of construction equipment do not often document their innovations in publications, most of the information contained in this data set comes from interviews held with employees of tractor shovel manufacturer and user firms who had been associated with the innovations studied. Interviewee recollections of dates of innovation commercialization have been checked against the dates of related advertisements that appeared in construction equipment trade journals.

The Original Tractor Shovel

The tractor shovel is a mobile, rubber-tired machine used for excavating and for the general handling of such bulk materials as earth, coal, and chemicals. A tractor shovel looks somewhat like a farm tractor with a large movable scoop mounted at the front end. Today, tractor shovels are produced in a wide range of sizes. Very large tractor shovels with massive 20 cu-yd scoops can be found working in open-pit mines, filling an entire truck with coal or ore with a single scoop. At the other extreme, one can find small tractor shovels in warehouses shifting various materials from place to place 1 cu yd at a time.

Development History

Prior to the development of a special-purpose machine known as the tractor shovel, a few firms built loading attachments for use on farm tractors. These scoops had limited mobility but were suitable for light material-handling tasks. One of the firms that manufactured such attachments was the W. M. Blair Manufacturing Company. In 1933, W. M. Blair was bought by an entrepreneur named Frank G. Hough. In 1939, for reasons not clear to those working with him, Hough decided to develop a specialized machine that could *only* be used for loading tasks but would be highly efficient at that function. There is no indication that Hough was spurred to undertake this task either by user requests for such a machine or user development activity.

Lowell Conrad, chief engineer at the Hough Company at that time, recalls that the development of the first tractor shovel was carried out by all the engineers then working at the company (only two or three!). The task took about six months and cost approximately $13,000 in parts and labor (engineers' wages were $200–$300 per month). Costs were kept down in part by obtaining heavy-duty tractor parts from International Harvester on consignment. Other parts were made by Lowell Conrad at night in a neighboring machine shop.

Commercialization

The tractor shovel that Hough and his engineers developed was called the Model HS and was first commercialized in 1939. Approximately 100 of the Model HS tractor shovels were sold from first commercialization until 1941 when production was stopped by wartime requirements.

In 1944 the Hough Company again began to produce tractor shovels, this time offering a small model (HA) suitable for unloading box cars. In 1946 the first competition appeared in the form of a three-wheeled tractor shovel produced by the Scoopmobile Company located in Oregon. In 1950 the Tractomotive Company of Ohio (later of Deerfield, Illinois) also produced a tractor shovel.

Side Lift Arm Linkage

The scoop of the original tractor shovel was attached to the tractor by a guide-frame linkage—the same sort of linkage used on a modern forklift truck. The linkage consists basically of two vertical rails attached to the tractor. The scoop is moved vertically up and down these rails. The side lift arm linkage that replaced it looks more like the linkage that attaches the blade to a modern bulldozer. In this linkage the scoop is attached to the tractor by two large horizontal beams that extend from the sides of the scoop to the sides of the tractor. The scoop is lifted by pivoting these beams around their point of attachment to the tractor.

The side lift arm linkage offers two great advantages to tractor shovel users. First, the pivoting motion that lifts the scoop also has a horizontal component that pushes the scoop slightly forward at the beginning of the lifting movement. This forward component of motion, called crowding, is very helpful when the operator is trying to scoop up hard-packed material. Second, the side lift arm linkage greatly reduces the overall height of the tractor shovel. In the older guide rail linkage, the guide rails were vertically fixed permanently, with their upper ends always at the height of the maximum vertical extension of the tractor shovel scoop.

Development History
Lowell Conrad, chief engineer of the Hough Company, conceived of, and developed, the side lift arm linkage innovation. Conrad recalled deciding to develop such a linkage as a result of a trip to a tractor dealer in Kansas City. The dealer told Conrad of the many underground mining operations in lead and limestone then existing around Kansas City. Existing tractor shovels could not be used in these mines because of the high clearance required by the guide frame linkage. The dealer emphatically told Conrad that he could sell many tractor shovels to these customers if the clearance problem could be eliminated.

Commercialization
In 1945 Hough was first to introduce side lift arm linkages on tractor shovels. Lowell Conrad estimates the total direct cost of the development work—given the staffing, salaries, and material costs of the day—at about $5000.

Side lift arm linkages were next commercialized by Scoopmobile on their Model C in 1948. Transco followed in 1950 as did Tractomotive.

Power Steering

The power steering systems used on tractor shovels are much like those used on cars and trucks. That is, they involve a hydraulic system that assists the steering efforts of the operator. Since the tractor shovel carries heavy loads on its front (steered) wheels, steering effort is high and the introduction of power steering reportedly increased tractor shovel productivity significantly.

Development History
In 1948 power steering was standard equipment on many types of heavy-duty construction equipment. The essential components of these systems were manufactured by firms such as Vickers and Garrison, specialists in hydraulic equipment. In 1947 Garrison came to the Hough Company and suggested they install power steering on their larger tractor shovels. They offered technical help and what was in essence a kit of components that could conveniently be adapted by Hough engineers to their equipment.

Commercialization
In 1947 Hough offered a kit based on Garrison components that users could install on their machines in the field. In 1948 Hough offered a factory-installed version of the Garrison system as an option on their four-wheeled drive (Model HF tractor shovel).

In 1948 the Dempster Company offered a Vickers hydraulic system on their Digster model; Scoopmobile offered power steering on its Model C.

Hydraulic Bucket Control

The scoop of a tractor shovel is emptied by rotating it until the open side of the scoop faces downward and the material carried simply falls out. Prior to hydraulic bucket controls, the bucket was attached to a pivot point below the bucket's center of gravity. On the release of a mechanical latch, the bucket simply flipped over in an uncontrolled manner and released the total contents. The hydraulic bucket control substituted a hydraulic piston and valve so that the operator could regulate the rotation of the bucket and thus dump a load partially or fully—a very useful capability. Hydraulic rotation of the bucket was also valuable in the digging of hard-packed material. An operator could wedge a lip of the scoop into the material and then rotate the bucket to break it loose.

Development History

The physical embodiment of the hydraulic bucket control was a hydraulic piston mounted between the bucket and a yoke fitted appropriately to the scoop lift linkage. It was developed by Lowell Conrad's engineering group at Hough in 1947. Since a source of hydraulic power was already on tractor shovels, development effort required to design and install the hydraulic bucket control—once the insight was available—was minimal in Lowell Conrad's recollection. Conrad estimates that it cost approximately $5000 in labor and materials to design and prototype the first hydraulic bucket control.

Commercialization

The hydraulic bucket control was first commercialized in 1947 on the Hough HLD Model. After Hough commercialized this innovation, other manufacturers of tractor shovels quickly imitated and offered functionally equivalent systems.

Fluid Transmission Coupling

As owners of manual transmission automobiles are aware, when a clutch slips, it rapidly wears out. Operators of tractor shovels found themselves often having to slip the clutch when they were trying to move heavy loads. As a result clutches on these machines often needed replacement after only a few weeks' use. The fluid transmission coupling is an innovation designed to solve this problem. In essence, it is a hydraulic component of the drive train that can absorb slip nondestructively. Tractor shovels equipped with it allow operators the same mechanical torque advantages formerly achieved by slipping the clutch, but without the associated clutch wear.

Development History

According to interviewees, frequent customer complaints and requests for replacement parts made all tractor shovel manufacturers very aware of the clutch wear-out problem. Since Scoopmobile engineers knew that fluid couplings had been successfully used to solve clutch-slippage problems on other types of construction equipment, it was natural for them to adopt the same solution.

Appropriate fluid couplings were available from suppliers as a standard component. Since Scoopmobile used Chrysler industrial engines in its tractor shovels, it was able to install Chrysler fluid couplings with a minimal development cost. (At this time, Scoopmobile's entire engineering department consisted of three people, at an average salary of $100 a week.)

Commercialization

In late 1948 Scoopmobile offered a fluid coupling on their Model C tractor shovel.

Planetary Final Drive

In the late 1940s tractor shovel manufacturers purchased heavy-duty truck axles from major suppliers and adapted these to their machines. These axles were not strong enough for some of the rough conditions encountered by tractor shovel users, and they often broke. The planetary final drive innovation was an ingenious idea that allowed manufacturers of tractor shovels to continue to use truck axles but to reduce the torque experienced by these and, thus, eliminate the breakage problem. This effect was achieved by installing a final gear reduction in the form of a planetary gear system in the hub of each driven wheel of the tractor shovel.

Development History

The principles of planetary gear systems have been well-known to engineers for many years. Harry Fielding, chief engineer of Scoopmobile, recalls that he developed the application of this principle to the problem of torque reduction in tractor shovel drive axles as a result of seeing an old steering wheel from an early Ford car in a junkyard. This steering wheel contained planetary drive-gear reduction in its hub. Fielding quickly developed planetary final drive for Scoopmobile tractor shovels and recalls that the direct cost of the development work as only several hundred dollars.

Commercialization

In late 1948 or early 1949 Scoopmobile was the first to commercialize planetary final drive on their Model CF tractor shovel. In 1953 Clark Equipment Company offered planetary final drive on their new line of tractor shovels (they made their entry into the business at this time). In 1953 Hough also offered planetary final drive.

Double-Acting Hydraulic Cylinders

The pistons of double-acting hydraulic cylinders can be moved both in and out by the application of hydraulic force. In contrast, the pistons of single-acting hydraulic cylinders can only be moved in one direction by hydraulic force. Until the innovation of double-acting cylinders, hydraulic pistons installed on tractor shovels were all of the single-acting variety. This meant, for example, that tractor shovel operators could lift the scoop of their machine with hydraulic force, but they were forced to rely on the weight of the scoop itself for any motion in a downward direction.

The introduction of double-acting cylinders gave operators increased control over the scoop of the tractor shovel and allowed them to apply increased downward force. This was very useful in many tasks—as in, for example, scraping ice from streets in winter.

Development History

Hough was the first company to introduce double-acting cylinders to tractor shovels. According to interviewees at that company, they were motivated by a particular sensitivity to the municipal market for street clearing. For this application it was quite clear that down pressure provided by the weight of the bucket only was not sufficient. It was also clear that increased down pressure would be useful in such tasks as breaking up the asphalt surface of roads. Cost of implementing the innovation was quite low because double-acting cylinders and the controls needed to operate them were standard products of the hydraulic supply industry. All that was needed was to install double-acting cylinders in the locations occupied by single-acting cylinders and to add appropriate reinforcement to affected linkage points.

Commercialization

Double-acting cylinders were first commercialized by Hough in 1948 on their Model

HM. The rest of the industry quickly followed and also commercialized the improvement.

Four-Wheel Drive

Four-wheel drive offers much the same advantages to users of tractor shovels as it does to the users of four-wheel drive trucks and similar equipment. In essence, it offers better traction, especially on rough terrain, and rough terrain was often encountered by tractor shovels being used on construction sites.

Development History

The development of a four-wheel-drive tractor shovel was technically straightforward—but quite costly. Although the engineering required was well understood and although the axles needed for four-wheel drive were available as standard components from manufacturers, much of the tractor shovel had to be redesigned in order to incorporate the four-wheel-drive feature. For example, many existing components had to be shifted to make room for the new drive train needed. Also, provision had to be made to allow the rear axle to oscillate so that it might keep better contact with the ground on rough terrain. Total direct cost to develop the four-wheel-drive tractor shovel is estimated by Lowell Conrad at $70,000.

Commercialization

In 1948 four-wheel drive was first offered commercially by Hough on the Model HF tractor shovel. In 1953 Scoopmobile followed. Today, four-wheel drive is a common feature of tractor shovels.

Torque Converter

A torque converter is a hydraulic mechanism used in transmissions that provides an effect equivalent to infinitely variable gearing within a narrow range. When used in the transmission of a tractor shovel, it enables operators to adjust the torque they apply to a task more precisely than can be done with manual transmission alone. Tractor shovels equipped with a torque converter need not also have a fluid coupling because the function of this device is also inherent in the torque converter. (See the earlier description of fluid coupling.)

Development History

Torque converters developed by Allis Chalmers had been used in construction machinery as early as 1947. Tractomotive, a manufacturer of tractor shovels, had a history of close association with Allis Chalmers, indeed, it was eventually acquired by that firm. If Tractomotive were already using Allis Chalmers' transmissions and engines (which seems likely, although we have no direct evidence), then adoption of the Allis Chalmers torque converter would have involved almost no development work on the part of Tractomotive. Design work necessary to integrate the Allis Chalmers torque converter with the Allis Chalmers engine and transmission would already have been done by that firm.

Commercialization

The torque converter was first offered as a commercial feature of tractor shovels by Tractomotive in 1951. In 1953 the Hough Company offered it on their Model HMC.

Articulation

Articulation like four-wheel drive involves major changes in the configuration of the tractor shovel. In effect, the entire machine is split in two at a point between the front and rear wheels and then reattached by means of a hinge. This hinge is controlled and flexed by means of hydraulic cylinders mounted on either side of it. Articulation eliminates the traditional steering system: The driver turns by bending the machine in the middle at the hinge point.

Articulation offers several advantages to the user. First, it provides a shorter turning radius. Second, it reduces maintenance costs and downtime related to, and caused by, steering mechanisms and their failure. Third, with articulation the rear wheels follow the same path as the front wheels, and both sets follow directly in the path of the front scoop, which can thus be used to clear the way.

Development History

Articulation was developed at the Scoopmobile Company. The direct motivation to the development work (according to Harry Fielding, chief engineer of that company) was inventory reduction rather than performance. Front and rear axles are the most expensive components of tractor shovels, and an articulated machine uses the same type of axle both front and rear. Articulation had been developed and patented prior to 1953 by a British manufacturer of construction equipment. Fielding claims Scoopmobile was unaware of the British patent when it did its own development work and only found out about it when conducting a patent search.

Commercialization

Scoopmobile was first to commercialize articulation on tractor shovels, introducing the innovation with their LD 10 model in 1953. Scoopmobile salesmen quickly became expert at graphically illustrating the advantages of articulation. Competitive machines would often embarrassingly fail to perform or mire down on customers' sites under conditions the Scoopmobile LD 10 proved able to handle. Despite this demonstrable superiority, competitors were relatively slow to adopt articulation. In part this was probably because articulated machines looked decidedly odd to the traditional eye; in part it was probably because Scoopmobile was a small regional company most of whose sales were restricted to the Pacific Northwest. Therefore, the advantages of articulation did not really offer a significant competitive threat in the major markets of other producers.

In 1962 the Euclid Company developed an articulated machine that used the basic method spelled out in the British patent. In 1964 Caterpillar, which did not begin to produce tractor shovels until 1959, introduced articulated machines, as did the Hough Company with their Model H120C. Today, all large tractor shovels use this innovation.

Power Shift Transmission

The power shift transmission is a form specially suited for the requirements of tractor shovel operation. All available gears are permanently in mesh, and each is mechanically linked to a separate clutch. Thus, if the transmission has four gears, it has four separate clutches. Selection of a gear in a power shift transmission simply involves engaging the proper clutch by the simple motion of a hand lever connected to a hydraulic actuator. All foot action on the part of the operator in the shifting process is eliminated.

On many tasks that tractor shovels perform, operators have to shift very frequently—as often as 10 times a minute. In tasks requiring frequent shifting, operator fatigue from that task significantly constrained tractor shovel productivity. This was graphically illustrated by the increased productivity shown by tractor shovels equipped with power shift transmissions.[1]

Development History

The first power shift transmission was developed by Clark Equipment Company in 1952 and 1953. Clark was a new entrant into the tractor shovel business, and they wanted the first models they offered to have a power shift transmission.

Lowell Conrad left Hough to join Clark and develop the power shift transmission; he estimates its development cost at $250,000.

Commercialization

Clark introduced the power shift on their new line of Michigan brand tractor shovels in 1954. This line of shovels was commercially very successful. Indeed, within two years Clark was selling as many tractor shovels as Hough—the firm that had traditionally dominated the industry. In 1955 Hough introduced a form of power shift transmission based on the GM Truckmatic drive in their HO model.

Note

1. "Construction Equipment: Ten Years of Change," *Engineering News Record* 170 (21 February 1963): 45.

DATA SET FOR ENGINEERING PLASTICS

The data set for engineering plastics examines innovations in engineering thermoplastic materials. Engineering plastic is the common term for materials that can compete with traditional engineering materials such as metals, wood, and glass from the standpoint of such properties as strength, temperature resistance, and ease of fabrication. Engineering thermoplastics are thus suitable for such applications as gears and motor housings—applications for which metals were traditionally used. Sample selection criteria for this data set will be found in chapter 3.

Polycarbonate Resins (Lexan)

Polycarbonate resins (better known in the United States under the General Electric trade name of Lexan) have several important properties that make them excellent engineering materials. They have high-impact strength, superior dimensional stability, transparency, and good electrical insulation qualities. They are also self-extinguishing—an important property where fire safety is at issue. These properties have made polycarbonate of great value in applications ranging from precision camera components (an application where dimensional stability is important) to football helmets (an application where toughness is critical).

Development History

Polycarbonate engineering plastics were developed independently by two firms: GE in the United States and Farben Fabriken Bayer AG of West Germany. Research work in both firms began about 1953. Commercialization (i.e., the sale of developmental quantities of the material manufactured in a pilot plant), however, was first achieved by GE; we, therefore, regard GE as the innovating firm.

Lexan polycarbonate resins were discovered by Dr. Dan Fox, a researcher at GE, through serendipity. In 1953 Fox joined a team of GE researchers working to develop an improved electrical insulation for magnet wire. Insulated magnet wire is a critical part of electrical motors and other apparatus manufactured by GE. Development of a thinner insulating material capable of withstanding high temperatures would allow the construction of better performing and smaller electrical motors and generators.

When Fox joined the research team, a family of polymeric materials had been discovered that had the proper flexibility, toughness, and resistance to high temperature, but all were somewhat degraded by water. Fox recalled some postdoctoral research he had conducted at the University of Oklahoma in which he had used guaiacol carbonate and found it extremely hydrolytically stable. He, therefore, decided to try to make a polymer based on this material. He experimented with bisphenol-A and started making a polymer by ester exchange with diphenyl carbonate. The resulting polymer was Lexan.

The polymer discovered by Dr. Fox was not considered the most promising route to a wire insulation of the desired properties and was put on the shelf until the completion of the wire insulation project in 1954. In 1954 the chemical development department of GE decided to make a polycarbonate resin to be used as a molding material—the first such material of its own GE would attempt to commercialize. Development of Lexan to the test-market stage was completed by 1958.[1]

Commercialization

General Electric began to test market polycarbonate resin in the United States in 1958; Farben Fabriken Bayer AG began to introduce the product in Europe in 1959. Given the independent research work of both firms in the polycarbonate field and given that both had independent patent positions, these two firms entered into an agreement not to contest each other's patents. Development cost for polycarbonate was approximately $10 million.[2] Sales of Lexan grew quickly: In 1960 approximately 500,000 lb were sold at a price of $1.50/lb; in 1969 approximately 31 million lb were sold at a price of $0.80/lb.[3]

Notes

1. National Academy of Sciences, *Applied Science and Technological Progress,* A Report to the Committee on Science and Astronautics, U.S. House of Representatives, GP-67-0399 (Washington, D.C.: U.S. Government Printing Office, June 1967), 35–37.

2. Author's estimate based on information supplied by Dr. Dan Fox, General Electric, Schenectady, N.Y.

3. Dirk Oosterhof, *Chemical Economics Handbook: Plastics and Resins,* 580.1120A. (Menlo Park, Calif.: Stanford Research Institute, March 1970), sections F and I.

Acetal Homopolymer Resins (Delrin)

In the United States, acetal homopolymer is probably best known by the Du Pont brand name, Delrin. Delrin is a nontransparent engineering plastic. The plastic has a regular structure and high crystallinity that gives parts made from Delrin high strength and rigidity, excellent dimensional stability, and resilience over a wide range of service temperatures and humidities and a wide range of solvent exposures. In addition, the plastic has excellent frictional properties, which allows the plastic to serve as a good mechanical bearing.

Developmental History

Delrin is a polymer of formaldehyde. The existence of formaldehyde polymers had been known since before the 1920s. Interest in them was limited, however, because they were felt to be inherently unstable. In 1947 A. Barkdoll, Jr., of Du Pont's chemical department, began to study formaldehyde monomer and discovered that the pure monomer sometimes spontaneously polymerized into a polymer with attractive properties. In the 1949–50 period a project under R. MacDonald was begun that was explicitly devoted to the development of formaldehyde polymers. In late 1952 the research looked so promising that the polychemicals department (one of Du Pont's major industrial subdivisions) put 60 men to work on the project. Up to 1960, Delrin R & D expenses were approximately $27 million.[1]

Commercialization

Du Pont invested $15 million in a plant at Parkersburg, West Virginia, capable of producing about 15 million lb of Delrin annually, and introduced it commercially in 1960. Du Pont is the sole producer of acetal homopolymer. Its high expectations for the commercial success of the plastic were not fully met, however, owing to the later commercialization of an acetal copolymer called Celcon by Celanese in 1963. (See discussion of acetal copolymer below for details.) In 1974 approximately 70 million lb of acetal resins were produced with one quarter of this being acetal homopolymer resin (Delrin). The sales price of Delrin was $0.95/lb in 1960 when the product was introduced and was $0.80/lb in 1974.[2]

Notes

1. Herbert Solow, "Delrin: du Pont's Challenge to Metals," *Fortune* 60, no.2 (August 1959): 116–19.
2. *Chemical Economics Handbook: Plastics and Resins,* 580.0121 (Menlo Park, Calif.: Stanford Research Institute, October 1975), sections B and E. The percentage of acetal resin production consisting of acetal homopolymers was obtained from *The Kline Guide to the Plastics Industry,* ed. James A. Rauch (Fairfield, N.J.: Charles H. Kline & Co., 1978), 56.

Acetal Copolymer (Celcon)

Acetal copolymer is a polymer of formaldehyde. It has slightly better properties with respect to heat and solvent resistance than does the closely related acetal homopolymer (Delrin) (see preceding entry).

Development History

Celanese Corporation is a basic producer of formaldehyde—the feed stock for acetal homopolymers and copolymers. Du Pont's demonstration in 1960 that a formaldehyde polymer with commercially attractive properties could be produced induced Celanese to accelerate its research in the area. Intensive research and development at Celanese—with Drs. Brown, Barting, and Walling essential to the effort—allowed Celanese to produce pilot-plant quantities of Celcon in April 1961 in Clarkwood, Texas.[1] A long and difficult court battle then ensued between Du Pont and Celanese over patents—Celanese finally won the case.

Commercialization

Du Pont's experience with the introduction of Delrin allowed Celanese to proceed to full-scale production rapidly, confident of Celcon's commercial attractiveness. Celanese's first plant for the production of Celcon went on-stream at Bishop, Texas, in January 1962.[2] Approximately 125 million lb of acetal resins were produced in 1974 by Du Pont and Celanese.[3] Approximately 35 million lb of this was exported; approximately 90 million lb was consumed in the U.S. market. Approximately three quarters of the total volume was acetal copolymer.

Notes

1. "Celanese Celcon Plant On Stream," *Modern Plastics,* 39, no. 6 (February 1962): 45.
2. *Chemical Economics Handbook: Plastics and Resins,* 580.0121A (Menlo Park, Calif.: Stanford Research Institute, October 1975), 580.
3. James A. Rauch, ed., *The Kline Guide to the Plastics Industry* (Fairfield, N.J.: Charles H. Kline & Co., 1978), 56.

Polysulfone Resin

Polysulfone is composed of phenylene units linked by three different chemical groups—isopropylidene, ether, and sulfone—each contributing properties to the polymer that are conventionally obtained through stabilizers or other additives. Polysulfone is a strong, rigid thermoplastic that can operate in high-temperature environments. The heat distortion temperature of polysulfone at 264 lb/sq in. is 345°F. Polysulfone also has a high rating for self-extinguishability. Its combination of characteristics has made it important in applications involving long-term service at high temperatures under load.

Development History

Polysulfone was developed by Dr. H. Farnum and Dr. Robert Johnson, researchers at Union Carbide Corporation. They were searching for a thermoplastic material that could withstand high temperatures—motivated by a finding of Union Carbide's marketing research that there was a market for an engineering plastic that was stable at up to 175°C. Farnum and Johnson had a good theoretical sense that phenylene units in a polymer chain would exhibit satisfactory high-temperature characteristics. They synthesized and analyzed 40 to 50 possible molecular structures before deciding on the presently commercialized polysulfone.

Commercialization

Polysulfone was commercialized by Union Carbide in 1965. Union Carbide remains the sole producer. Production began in a plant constructed in Marietta, Ohio, capable of producing 10 million lb/year. The initial price was $1.00/lb.[1] In 1976 production was approximately 12 million lb with a market price of approximately $22 million.[2]

Notes

1. "New Engineering Thermoplastic—Polysulfone," *Modern Plastics* 42, no. 9 (May 1965): 87–89, 196.
2. James A. Rauch, ed., *The Kline Guide to the Plastics Industry* (Fairfield, N.J.: Charles H. Kline & Co., 1978), 55.

Modified Polyphenylene Oxide (Noryl)

Noryl is a thermoplastic with outstanding dimensional stability at elevated temperatures. It is hydrolytically stable and has both excellent dielectric properties and chemical resistance. It is widely used in automotive and appliance applications.

Development History

Noryl was developed by General Electric researchers and is a commercially successful modification of an earlier GE polymer, polyphenylene oxide (PPO). Research that led to PPO was begun by A. S. Hay in the mid-1950s in the GE Research Laboratory in Schenectady, New York, where he was working on the oxidation of organic compounds, particularly phenols. According to Hay his research had no application in mind. In 1956 he discovered polymerization of phenols by oxidative coupling—a new chemical technique for synthesizing plastics.

Because of GE's then-ongoing work on Lexan, Hay's discovery was not developed further until 1960. In 1960 an effort was begun by J. R. Elliot of the chemical development operation to find an economical means of producing the product commercially.

In 1965 a pilot plant was ready to produce PPO and the product was commercialized. Various applications such as surgical instruments and appliance parts were made with PPO, but by 1957 it was clear that PPO was a commercial failure. It had proven hard for molders to process because it required specialized molding machinery and a drying step.[1] As the commercial failure of PPO became clear, work was begun to modify the material. Noryl was the result of this research: an alloyed PPO that is easy to process.

Commercialization

Noryl was introduced commercially in 1968. Its sole manufacturer is GE. In 1976 approximately 95 million lb were sold with a sales price of approximately $90 million.[2]

Notes

1. National Academy of Sciences, *Applied Science and Technological Process,* A Report to the Committee on Science and Astronautics, U.S. House of Representatives, GP-67-0399 (Washington, D.C.: U.S. Government Printing Office, June 1967), 37.
2. James A. Rauch, ed., *The Kline Guide to the Plastics Industry* (Fairfield, N.J.: Charles H. Kline & Co., 1978), 55.

DATA SET FOR PLASTICS ADDITIVES

The data set for plastics additives contains information on innovations for two types: plasticizers and ultraviolet stabilizers. Specific sample selection criteria will be found in chapter 3. Data on all innovations listed in that sample will be found here, with the exception of four coded NA in chapter 3, Table 3–8. In these instances we could not find needed data after diligent research.

A plasticizer is a material that is incorporated mechanically into a plastic to increase its flexibility and workability. Without plasticizers polymers such as polyvinyl chloride (PVC) are hard and brittle; with plasticizers they become softer, more flexible, and easier to process. A UV stabilizer is a compound that protects plastic from the degrading effects of UV light. In the absence of UV stabilizers, polymers exposed to UV show loss of physical properties and discoloration, often accompanied by surface crazing (the formation of many fine cracks on the surface of a plastic), embrittlement, and chalking.

In chemistry-related fields, *Chemical Abstracts* is a major resource for the type of study conducted here. As a cross-check on our findings regarding the first to develop innovations researched, we searched *Chemical Abstracts* for several years prior to the date of each innovation to check for any application earlier than that we had identified by interview. Market size and development cost estimates given by interviewees in some of the innovation histories that follow are approximate and informal. Development cost figures, when provided, refer to direct costs only.

PLASTICIZERS

Butyl benzyl phthalate

Butyl benzyl phthalate is a plasticizer used in polyvinyl chloride (PVC). Its main advantage over earlier plasticizers used with PVC is that it fuses with PVC resins at a much lower temperature. This meant that PVC could be processed on standard rubber-processing machines that operate at 110° to 130°C rather than on special PVC milling machines that operate at 150° to 160°C. Rubber processors were thus able to change over from rubber to PVC processing without purchasing new machinery.

Development History

In the 1930s Bayer took out a patent for butyl benzyl phthalate as a plasticizer for cellulose nitrate. A Monsanto research team under the leadership of Joe Darby (manager of the plastic applications laboratory) reasoned that butyl benzyl phthalate might also be a good plasticizer for PVC. When they discovered the attractively low temperature at which butyl benzyl phthalate could be blended with PVC, they took it to the marketing department to be considered for commercialization. Monsanto also took out process patents in 1946 to cover improved means of producing the plasticizer.

Commercialization

Monsanto introduced butyl benzyl phthalate in 1946 and marketed it to rubber and PVC products. In 1974 approximately 80 million lb of the plasticizer was sold at a market price of approximately $28 million. Monsanto interviewees estimate the cost of the development of the plasticizer at approximately $500,000 to $1 million.

2 ethyl hexyl di phenyl phosphate

2 ethyl hexyl di phenyl phosphate is a plasticizer that equaled the desirable cold flex and volatility characteristics of competitive plasticizers and also imparted flame retardancy to plasticized polyvinyl chloride (PVC). In addition, the plasticizer is nontoxic and has Food and Drug Administration (FDA) approval for use in food-packaging films, a major application.[1]

Development History

In 1945 Union Carbide introduced a PVC insulation material that was plasticized with di octyl phthalate. This product showed excellent cold flex characteristics and Monsanto was anxious to match it or exceed it. Monsanto, therefore, began looking for a low toxicity, flameproof plasticizer that would be equivalent to di octyl phthalate in cold flex and volatility. The product they developed succeeded in combining the good cold flex properties of the di octyl phthalate with the excellent flame-proofing and solvating properties of the aryl phosphates to give a product that generally has many of the best properties of both compounds.

Commercialization

2 ethyl hexyl di phenyl phosphate was commercialized in 1947 by Monsanto. There is no competitive producer of this product in the United States, but Monsanto itself has since developed a second product of this type—iso decyl di phenyl phosphate—that provides even better cold flex and volatility products. These two plasticizers have tended to replace tri alkyl phosphates and tri butyl phthalates in the marketplace.

Note

1. J. Kern Sears and Joseph R. Darby, *The Technology of Plasticizers* (New York: Wiley, 1982).

Citroflex Plasticizers

Citroflex-type plasticizers are used for vinyls and cellulosics. Examples of such plasticizers are: tri butyl citrate and acetyl di butyl citrate. The principal advantage these plasticizers offered over existing plasticizers in 1957, the year of their introduction, was FDA approval to use them to plasticize films used to package oily and greasy foods. Phthalate plasticizers, by way of contrast, only have FDA approval for use in films to package high-water–content foods.

Development History

Pfizer Corporation, a producer of citric acid, was anxious to develop uses for that acid. Also, it was anxious to move out of the phthalic ester plasticizer business because it was basic in neither the anhydride nor the alcohol components of this product. Both problems were addressed by a research project that attempted to develop the citroflex plasticizers. The work proceeded from 1953 to 1957 and resulted in the development of a range of citroflex esters. The costs of development per ester were estimated by a participant in the research project as approximately $125,000. Toxicological testing of each ester was estimated at $150,000 to $250,000.

Commercialization
Pfizer introduced the citroflex-type plasticizers in 1957. It is the only supplier of these esters to the present day. Dollar volume of sales in 1974 is held in confidence by Pfizer.

Note

1. Arnold L. Baseman, "A Compounder's Guide to . . . Plasticizers '65," *Plastics Technology* 11, no. 10 (October 1965): 37–44.

Di N undecyl phthalate Plasticizers

The plasticizer di N undecyl phthalate is one of two long alkyl chain phthalates that are widely used for plasticizing PVC cable wiring designed to operate at 75° C and above. These plasticizers are superior to the branched tri decyl phthalates formerly used for this purpose in three major ways: (1) they provide a superior cold flex at low temperatures; (2) they fuse with PVC at a lower temperature than the earlier plasticizers, which eases processing requirements; (3) they are more compatible with PVC than were earlier plasticizers, which tended to bleed at flexing points in the cable.

Development History
The need for a good, highly compatible plasticizer suitable for use with PVC subjected to high temperature was widely known within the plasticizer industry. From 1967 to 1970 the Monsanto plasticizer applications laboratories worked to develop such a product. The approximate cost of the research over the three-year development period was between $500,000 and $1 million.

Commercialization
The di N undecyl phthalate plasticizers were introduced commercially by Monsanto in the early 1970s. Monsanto has requested that its sales and market share be kept confidential.

Tri melitate Plasticizers

Tri melitate plasticizers are primarily used to plasticize polyvinyl chloride (PVC). The product had a lower volatility than previous plasticizers and thus reduced application problems such as the fogging of automobile windows by plasticizers volatilized from automobile parts. The new plasticizer also offered improved cold flex properties.

Development History
The precursor to tri melitate plasticizer was provided by the Amoco Company in 1961. In that year Amoco built a plant capable of producing 2 million lb of tri mellitic anhydride per year. As part of the effort to develop markets for its product, Amoco sent samples to at least three chemical companies suggesting that the product might be a component of a good plasticizer. Monsanto, Pfizer, and W. R. Grace all added alcohol to the sample to make tri mellitic esters and tested these as plasticizers.

Commercialization
On observing the good properties of tri mellitic esters, Monsanto, Pfizer, and W. R. Grace all commercialized the chemical as a plasticizer in 1961. In 1974 approximately 23 million lb of the plasticizer were sold by all three companies together.

Some $100,000 to $250,000 was spent on developing the new stabilizer. The market size for the innovation about 1970 was approximately $300,000 per year.

ULTRAVIOLET STABILIZERS

2:4 dihydroxy benzophenone

Polymers such as polystyrene and polyvinyl chloride are particularly susceptible to UV light in the 290 to 400 nm region. This UV light causes breakdown of the chemical bonds in the plastic, which in turn causes the plastic to deteriorate. Unprotected plastics may, for example, discolor and become brittle in the sun.

Benzophenone compounds were the first effective UV stabilizers on the marketplace. Typically, a PVC stabilized with a benzophenone compound would have a useful life one hundred times greater than that of unstabilized polyvinyl chloride in outdoor applications.

Development History

In the late 1930s or early 1940s Dow Chemical Company researchers patented 2 hydroxy 5 chloro benzophenone as a UV stabilizer. This compound proved to be only a weak absorber of UV light and gave a strong yellow color when used. It was not successfully developed commercially by Dow as a UV stabilizer for plastics.

I. G. Farben, a German firm, manufactured plastics of all sorts as well as a wide range of additives. During World War II, assets of I.G. Farben in the United States were sequestered by the U.S. Government. Employees of General Analine and Film (GAF), operator of the sequestered assets, found a considerable amount of data in the former I.G. Farben laboratories on UV-active compounds. A team of GAF researchers, Dr. F. Newmann, Dr. McKay, and Dr. Albert Strobel, began a program to develop a range of stabilizers for cellulose acetate. The team investigated a whole range of compounds found to be UV-active and determined that 2:4 dihydroxy benzophenone was an excellent stabilizer. (According to Dr. Strobel, at the time the GAF team did not know of Dow Chemical Company's earlier work on halogenated 2:5 benzephenones.)

Commercialization

General Analine and Film began commercial production of its first UV stabilizer sometime between 1948 and 1950. The total market volume of benzophenone-type stabilizers was perhaps $10 to $15 million per year in 1973. Dr. Strobel estimates that the cost of development, including monies spent on developing a production process, at about $1 million. The second producer of benzophenone UV stabilizers was American Cynamid.

Ethyl-2-cyano 3:3 diphenylacrylate

Acrylate UV light stabilizers are used in polar polymeric systems. Acrylates have replaced benzophenones in applications where colorlessness is critical. Unlike benzophenones, they do not produce a yellowish color over time.

Development History

The acrylate group of ultraviolet stabilizers was developed by GAF as part of a program to produce new UV stabilizer systems for the plastics business. The research began in 1947 and continued until 1952.

The idea for the acrylate group of stabilizers was developed by Dr. Albert Strobel of GAF through his knowledge of dye chemistry. As a result of experiments on dyes, he knew that hydroxy benzaldehyde and cyanoethyl acetate reacted to give a dye that was extremely light-stable and a powerful absorber of UV light. Dr. Strobel realized that if he could alter the molecule to remove the dye properties while retaining the light stability and the UV-absorbing properties, he would have a good UV stabilizer. Through extensive research he was able to achieve this result.

Commercialization

Acrylate UV stabilizers were commercialized in 1952 by GAF. On the whole they have been very successful commercially, replacing benzophenones in applications where colorlessness is critical in polar polymers. In general-purpose applications, however, they have not replaced benzophenones because they are more expensive on a cost-performance basis. In 1973 the sales volume of acrylate stabilizers—approximately 1/3 of 1 million lb/year—made them probably the third largest UV stabilizer group in volume terms. (In that year benzophenones sold approximately 2 million lb and benzotriazoles sold approximately 500,000 to 1 million lb. The market value of 1/3 of 1 million lb of acrylate stabilizer is approximately \$2 to \$3 million.)

2 hydroxy 4 dodecyloxy benzophenone

Polyolefins are a commercially important plastic that absorbs ultraviolet light strongly in the region of 300 Å to 310 Å. The absorption of this energy causes the polymer chains to break; this in turn causes surface crazing, embrittlement, chalking, discoloration, and loss of physical properties such as impact and tensile strength. 2H 4D benzophenone was the first colorless stabilizer that was compatible with polyolefins.[1] Prior to the development of this stabilizer only filled pigmented polyolefins could be used out-of-doors and even these were not as stable as was desired. Currently about 70% of all UV plastic stabilizers are used in polyolefins.

Major uses of UV-stabilized polypropylenes are in fibers for carpeting and upholstery and the like. Typically, the addition of a stabilizer extends the life of polyolefin 10 to 20 times in outside duty.

Development History

Most experts in the field of UV stabilizers were aware that a 4 long-chain alkoxy-substituted hydroxy benzophenone would be a good stabilizer for polyolefins. The major problem in producing such a compound was to economically alkylate the 4-position OH group while leaving the 2 OH group unreacted. The problem was solved by researchers at Eastman Kodak, who in 1958 took out a patent for 2 hydroxy 4 dodecyloxy benzophenone.[2] Dr. G. Arick of Eastman states that this product was developed for internal use and that Eastman Kodak is a major user of its own product.

Commercialization

Eastman Kodak first introduced the innovation commercially in 1960. Although they do sell the product, they also consume a substantial amount in-house. Eastman

Kodak's first competitor was American Cyanamid, who in 1961 introduced 4 octoxy 2 hydroxy benzophenone.

Notes

1. Note that polar benzophenones had been produced by GAF in the early 1950s, including 2 hydroxy 4 methoxy benzophenone. This was an excellent stabilizer, but it was incompatible with polyolefins.
2. U.S. Patent No. 2,861,053.

Nickel Complexes

Nickel complexes are used primarily to stabilize polyolefin polymers with respect to ultraviolet light. They have a significant advantage over previously available stabilizers for this purpose in that they simultaneously provide a site to which dye can adhere. Use of nickel complexes thus made it possible for the first time to dye polyolefins in strong colors. (Untreated polyolefins are not sufficiently polar to accept conventional dispersion dyes.)

Nickel complexes are synergistic in their effect with benzophenone UV stabilizers. When used together, these two compounds give 4 to 10 times the protection provided by either stabilizer used alone.[1] Although benzophenones are strong absorbers of UV light and thus protect the polymer, the nickel complexes act by a different mechanism. They act to quench groups on the polymer chain that are excited by UV light, thus preventing breakage of the molecule.

Development History

The nickel complex UV stabilizers were developed by Ferro Corporation. Ferro is a company that specializes in producing additives for plastics and paints. They do not produce the actual polymers themselves.

In the late 1950s Ferro engaged in a research effort to find additives in the polypropylene field in order to increase their product range and break into a new market. A. M. Nicholson of Ferro's research department headed a team that investigated 1400 different compounds for their properties with respect to polypropylene. The discovery that certain nickel compounds acted as dye sites was serendipitous. Ferro Corporation patented the most promising nickel compounds in 1960.[2]

Commercialization

Ferro Corporation commercialized the nickel complexes for use as stabilizers and dye sites in polyolefins in 1962. Ferro's first competitor was American Cyanamid.

Notes

1. Arnold L. Baseman, "UV Stabilizers for Plastics," *Plastics Technology* 10, no. 4 (April 1964): 30–35.
2. U.S. Patent No. 2,971,940 and No. 2,971,941. These patents, granted to A. M. Nicholson, C. H. Fucksman, and S. B. Elliot, were assigned to Ferro Corporation.

P methoxy benzylidene malonic acid dimethyl esters

P methoxy benzylidene malonic acid dimethyl ester ultraviolet light stabilizers were designed to compete with, and to be superior to, the acrylate stabilizers. They absorb UV in the shortwave-length region of the spectrum and thus give a high degree of protection to polar plastics such as polystyrene and polyurethane. The intrinsic light stability of the compounds and their absorptions on the low end of the spectrum give a colorless product that shows little yellowing owing to side reactions such as can occur with many of the benzophenone compounds.

Development History

P methoxy benzylidene malonic acid dimethyl ester UV light stabilizers were developed at American Cyanamid. This firm has an ongoing program to develop new and improved stabilizers for polypropylene and other polymers. A major part of this work consists of screening UV light-active compounds in order to determine their efficiency as stabilizers and their suitability in plastics systems.

Dr. Suret Susi, and American Cyanamid researcher, became aware through a survey of patent literature that the benzylidene types of materials might possibly be suitable UV stabilizers. He then prepared the p methoxy benzylidene malonic acid dimethyl ester compound and evaluated its properties as a stabilizer. A patent was applied for in April 1964.

Commercialization

Commercial production of p methoxy benzylidene malonic acid dimethyl esters began in 1964. Dr. Susi estimates that approximately $100,000 to $250,000 was spent on developing the new stabilizers.

2:4 di t butyl phenyl 3:5 di t butyl phenyl 4 hydroxy benzoates

2:4 di t butyl phenyl 3:5 di t butyl phenyl 4 hydroxy benzoates are UV stabilizers for polypropylene. They protect the polymer by absorbing ultraviolet light as does benzophenone, but they also react to stabilize polypropylene by a method that is not entirely understood. As a result this compound is claimed both to give enhanced life to polypropylene when judged relative to competitive UV stabilizers and to act as an antioxidant as well.

Development History

The UV stabilizer 2:4 di t butyl phenyl 3:5 di t butyl phenyl 4 hydroxy benzoate was developed by Dr. E. J. Smutney of Shell Corporation. Shell was a major manufacturer of polypropylene and wished to develop a good UV stabilizer in order to extend its market. In 1963 Dr. Smutney took out a patent on the innovative UV stabilizer.[1]

Commercialization

Shell Corporation did not commercialize the stabilizer. Although it knew it was a good product, it apparently could not produce the substituted acid precursor cheaply enough to make it a commercial success. Shell, therefore, approached several firms, including Ferro Corporation, with the product.

Ferro, a manufacturer of plastic additives, took a license from Shell to produce the innovation and developed an economical way of preparing the precursor acid for the stabilizer. This was patented[2] and allowed Ferro to produce the product at a commercially acceptable cost. Bill Meek of Ferro's research department states that he found a brief reference in a British journal to a carboxylic acid preparation that worked marginally well. He then improved the process by use of superior solvent chemistry. Ferro commercially introduced the product in December 1973. At present there is no competing commercial product. The cost to develop the product was approximately $25,000 to

$100,000. The cost to develop the process was approximately $100,000. The innovation has had some success in replacing benzophenones and benzotriazoles.[3]

Notes

1. U.S. Patent No. 3,112,338.
2. U.S. Patent No. 3,825,593.
3. Stephen C. Stinson, "Chemicals and Additives Today: The Pace of Development Quickens," *Plastics Technology* 18, no. 7 (July 1972): 35–49.

Zinc Oxide and Zinc diethyl dithio Carbamates

Zinc oxide and zinc diethyl dithio carbamate stabilizers are used in heavily pigmented plastic products. These products benefit only slightly from organic ultraviolet stabilizers since degradation occurs only at the surface of the product where there is only a small concentration of the stabilizer. The diethyl dithio carbamate acts synergistically with the zinc oxide giving a performance that is equal to, or better than, the performance provided by organic UV stabilizers at a lesser cost. Manufacturers claim that the life of pigmented plastics can be increased by 2 to 10 times when compared to plastics using titanium dioxide pigment and organic stabilizers.[1]

Development History

The zinc oxide and zinc diethyl dithio carbamate stabilizers were developed by two researchers at the firm of Debell and Richardson under the sponsorship of the International Lead and Zinc Research Organization. Stan Margosiak and Barry Baum of Debell and Richardson knew that zinc oxide had been used as a stabilizer for paints and that zinc diethyl dithio carbamate had been known to have antioxidant properties in rubber. This lead them to experiment with the effects of these two compounds in plastics. Debell and Richardson had been working on zinc stabilizer systems since 1967. A total cost of this particular project was about $100,000 to $200,000. The major costs involved testing the stabilized plastic systems.

Commercialization

The International Lead and Zinc Research Organization made the research results on the UV stabilizing properties of zinc compounds available to all its members. The compounds required were already produced by some members: New Jersey Zinc Company in Bethlehem, Pennsylvania, produces zinc oxide; zinc diethyl dithio carbamate stabilizers are produced by R. T. Vandervuilt Company in Norwalk, Connecticut. Thus, no commercialization expense had to be incurred by these firms. The value of the compounds in the UV stabilization of plastics was simply publicized to the plastics industry.[2]

Notes

1. Robert E. Hunt, "Chemicals and Additives '70," *Plastics Technology* 16, no. 7 (July 1970): 39–45.
2. D. S. Carr et al., "Zinc Oxide Stabilization of PP Against Weathering," *Modern Plastics* 47, no. 5 (May 1970): 114–18; D. S. Carr et al., "UV Stabilization of Zinc Oxide with Thermoplastics," *Modern Plastics* 48, no. 10 (October 1971): 160–61.