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The Application of Radiation Technology in Industrial Processes

Current and Future Perspectives

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The development of nuclear power has been responsible for many by-products, among them radioactive fission products. In the late 1940's and early 1950's considerable efforts were made to develop industrial processes that could make use of the fission products in large quantities. Although some fission products are utilized today, the scale does not approach the quantities that will be produced in a nuclear economy. The efforts have not been a failure, however, and the research to develop industrial processes has created markets, not for the fission products as one had hoped, but for the radioisotope Cobalt-60 produced by neutron capture in a nuclear reactor, and for accelerators — machines that produce radiation in a controlled manner. Success in finding uses for the major fission products may yet come, as research continues in the radiation chemistry and radiation biology fields.

Radiation processing is now a vigorously expanding area because of sharp increases in the reliability of electron beam generators, sharp drops in the unit cost of both electron beam power and electron beam energy, significant advances in radiation chemistry leading to lower dose requirements and increased engineering knowledge and practical experience.

The principal reasons for its bright future promise arise from expectations of further sharp decreases in the unit cost of electron beam energy and from the recent successful adoption of radiation on a large scale for cross linking of telephone wire insulation in the United States.

CURRENT STATUS

At this time there are more than a hundred electron beam generators and about thirty Cobalt-60 systems in routine industrial use. The market value of products treated or produced by ionizing radiation methods is well above $ 200 000 000 per annum. Let us go down the list briefly:

* This article is taken from an address delivered to the Nordic Society for Radiation Research and Radiation Technology in Helsinki, Finland.

RADIATION STERILIZATION OF DISPOSABLE BIOLOGICAL AND MEDICAL SUPPLIES – This is the oldest industrial application. It was first successfully applied in 1956 when machines cost $ 25 000 per kW and the cost of electron beam energy ran as high as $ 50 per kWh. A good deal of the high unit energy cost resulted from the low reliability of the 3 MeW van de Graaff and the 4 MeV linear accelerator first used in industrial practice. Despite the very high cost of radiation energy, however, the products provided enough advantages in packaging and customer convenience to permit them to capture 80% of the market with a high priced product. Ethicon, the first commerical organization in this field in the U.S., and its parent company Johnson & Johnson, soon shifted to gamma sources in order to employ a simpler, more reliable radiation technology. Since then, the developments in linac radiation sterilization methods by Risø, the success achieved industrially in providing reliable radiation sterilization services with a linac, and the improvement in linac technology and cost all combine to suggest that the role of Cobalt-60 as the principal radiation sterilization tool is threatened.

RADIATION CROSSLINKING OF POLYMERS – This is by far the most successful of the radiation applications. Industrial success in the radiation crosslinking of polyolefins for wire insulation and heat shrinkable connectors was first achieved by Raychem with the old General Electric Resonant Transformers. The success of W.R. Grace with its heat shrinkable Cryovac Type L film was also first achieved with the same machine at about the same time. Dose requirements to obtain the desired modifications have since dropped by at least 50% in both cases, and the cost of electron beam energy has decreased by 90%.

As for wire and cable, almost every major supplier of a product with crosslinked polyethylene or polyvinyl chloride has an irradiated product in its catalogue. The market is broad enough so that one company now supplies a PVC molding powder specially formulated for radiation-crosslinking. The Western Electric Company has begun production of telephone wire on a massive scale using a radiation-crosslinking technique; this achievement will be referred to later.

Two other crosslinking processes have come into prominence in the past five years: the radiation vulcanization of sheet rubber and foamed radiation-crosslinked polyethylene sheet. The first process is employed by Firestone in the U.S., and the second results from pioneering efforts by Sekisui Chemical Co. and Toray Products Co. of Japan, and Expanded Rubber Products in the United Kingdom. The current production rates in Japan are at a rate of 5 000 tons per annum, with Sekisui making about two-thirds of the sales. Sekisui is in the process of doubling its radiation processing capacity for manufacturing and marketing the product in the United States and Europe.

The irradiated product is far superior to the non-crosslinked polyethylene foam. The latter has an uneven, relatively open pore structure and an irregular surface, and is limited to use at temperatures below 75°C. The irradiated product, even when expanded thirty times in volume, has a smooth surface, uniform closed pores, and good resilience and recovery. The product is sold for use as crash padding in the Toyota, as a trunk liner in the Datsun, as a lining in cyclists' helmets, for toys, games, camping equipment, floor mats, and as a stuffing and stiffening in feminine wear. It can be laminated to other materials and a small but promising application is a laminate with wood to provide a flooring that will reduce noise levels; it can be cemented directly to a concrete floor.

Another material of some interest is prevulcanized natural rubber latex. French scientists have been working on this process over the past ten years, and have developed a product called Precurtex. It is produced by irradiation of the latex with a small dose of gammas or electrons. The final forms can be manufactured in existing equipment by evaporation of the serum at 70°C. The conventional process requires higher temperatures and the addition of vulcanizing and accelerating agents.

DURABLE PRESS FABRICS – Beginning production in 1966 with cotton fabrics, Deering-Milliken in the United States is now processing over 50 000 000 meters per year of VISA, a polyester-cotton fabric by a radiation-induced grafting method. The product is a durable press fabric with excellent soil release properties. It is sold principally to manufacturers of uniforms, overalls, etc. whose customers use commercial laundry services (hotels, garages, etc.). The product is made by padding the fabric with a vinyl monomer containing a methylol group, and subjecting the wetted fabric to electron irradiation. It is then padded with the soil release agent which is probably a prepolymer composed of acrylic and meth-acrylic acid. There are sufficient numbers of active grafting sites remaining from the irradiation so that the prepolymer is chemically "tacked" onto the fabric. The fabric is sent to the manufacturer who forms it into a garment. The finished garment receives its permanent press characteristics after it is pressed at 165°C for twelve minutes. The condensation reaction between the methylol group and the fiber produces the necessary crosslinks. An additional benefit is that the waste effluents from the plant have been reduced since no zinc chloride catalyzed treatment is required as in the conventional durable press processes.

RADIATION-CURED COATINGS – Almost every dashboard made by Ford Motor Company in the United States passes through an electrostatic spray coating machine and an electron beam curing. Other automobile parts also go through on a production basis and more are expected to follow. Despite the Ford success in producing an excellent and inexpensive substitute for the corresponding metal parts, the Ford experience has not been successfully followed by others.

There has been a discernible change since 1973, however. A plant in Switzerland and a plant in the United States with a capacity of almost 10 000 000 square meters per year for coated wood panels are being planned and two additional plants in Europe to produce radiation-cured coatings were being discussed in 1973.

The upsurge in interest seems to arise from pollution problems associated with heat-cured coatings. Ultraviolet-cured coatings are proving to be a formidable competitor for thin, clear coatings. But if the coating must be heavily pigmented or thick, then electrons may have a decisive advantage.

WOOD-PLASTIC COMPOSITES – For all practical purposes, there is only one producer, Arco Chemical in the United States, and only one product, parquet flooring. That company is producing some 300 000 square meters per year and adding to its ^{60}Co capacity. Thus Arco Chemical is succeeding on a modest and expanding scale in the only gamma process of significance which is not biological in nature, but there is little evidence of other industrial interest.

RADIATION DEGRADATION – About five years ago, Union Carbide Corporation decided to market polyethylene oxide for a wide range of applications, which, in turn, required a wide spectrum of molecular weights. Rather than adjust processing conditions to provide the molecular weight requirements of each application, UCC decided to produce a high molecular weight product under constant plant conditions and to submit the product to an inexpensive degradation to meet individual customer needs. A gamma-induced chain reaction in the presence of oxygen was to serve as the degradation step. A special irradiation facility was designed and construction initiated, but the plant had not gone into operation by 1973, as the market had not yet developed.

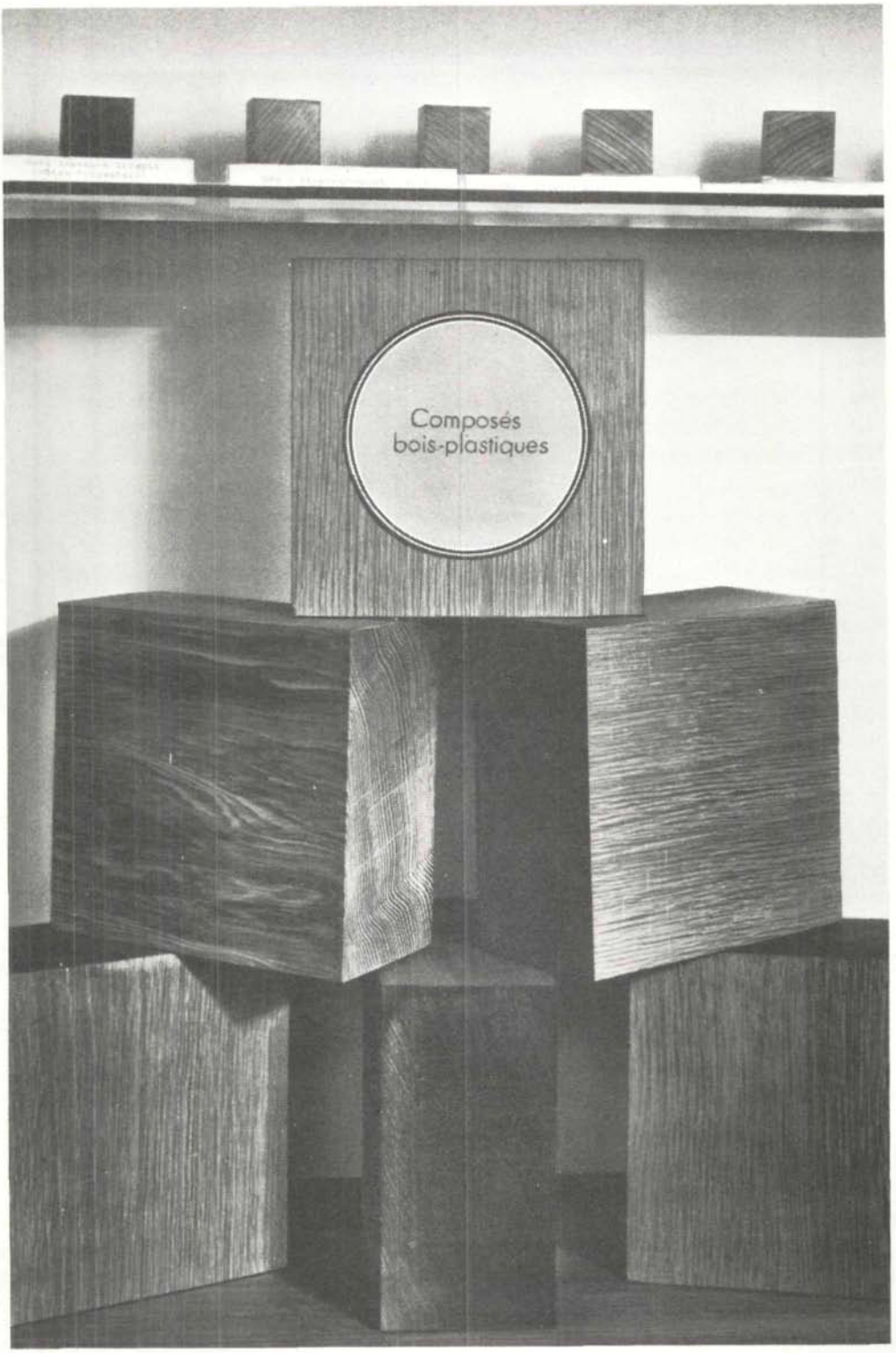
Radiation degradation is being turned to advantage by Columbia Research Corporation, a vendor of electron beam services. They are degrading waste polytetrafluoroethylene (PTFE) molding powder by electron-irradiation in air. The product is then used in spray lubricants. Their business in this area is surprisingly good; almost every producer of PTFE passes its scrap through Columbia's beam. Nevertheless this is still a low-volume application.

More important is the possibility that the UCC approach of manufacture and degradation may be applied successfully to the technology of polypropylene, which has a large sales volume. I believe that the approach deserves detailed consideration which it has not yet received.

There is another radiation degradation project in progress which concerns the electron irradiation of wood chips prior to storage and subsequent conversion to pulp. It is well-known that ionizing radiation kills insects, fungi and bacteria, and also that ionizing radiation degrades wood. Thus irradiation of wood chips should delay their spoilage and decrease the energy required to convert them into pulp. When the cost of the energy required to obtain these added advantages falls below the financial gains to be derived from them, radiation becomes a profitable and practical tool at the pulp mill. Radiation Development Co., Ltd. of Canada has installed two accelerator systems at the Georgia-Pacific Plywood mill near Albany, Oregon, and processed more than 10% of the plant's production. For the present Georgia-Pacific has rejected the RDCL process as effects obtained in the laboratory have not been obtained in the field in a reproducible way. If this performance can be improved about 2 000 pulp mills throughout the world become potential customers for what could be the biggest radiation application by any standard of measurement (production volume, kilowatts, and product value).

CHEMICAL SYNTHESIS – This has been the source of considerable disappointment to those who follow developments in radiation processing. Aside from the production of about 1 000 tons per annum of ethyl bromide by Dow Chemical Company, none of the proposed radiation-initiated chemical syntheses have been practiced on an industrial scale. One recent development suggests a favourable turn of events. A plant is now under construction in Japan to produce a prepolymer which will be a principal component of a paint formulation. (This is not to be confused with the electron beam curing of paint). The paint component is produced by a reaction initiated by electron irradiation; the paints based on it can be cured by thermal, UV, or irradiation methods.

These pieces of wood are processed by irradiation in the Centre d'Application des Rayonnements ionisants CAPRI in France. Photo: Pierre Jahan ▶


Composés
bois-plastiques

MISCELLANEOUS – Most of the applications described involve relatively low-volume production. There are several other applications which are conducted at an even lower scale. These include battery separators produced by radiation-induced grafting, a laminate of metal foil and a film composed of polyethylene and an acrylic acid graft, radiation crosslinked fasterners which expand on heating, irradiated quartz and pearls for jewelry, and so on. These represent some success in ingenuity and marketing, but none of them is likely to influence the field.

WESTERN ELECTRIC – Looking back at the list of products and processes, almost all of the applications in actual industrial practice are relatively old and wellknown. Until now, one might have concluded that new industrial applications would develop rather slowly due to the state of the art, the state of the economy, and the state of mind of industrial management. This conclusion now would appear to be too pessimistic.

The main reasons for this change can be found in the recent decisions and actions of Western Electric Co., the manufacturing arm of the American Telephone and Telegraph Co. In 1973 Western Electric began the production of telephone wire with radiation-crosslinked PVC insulation at the rate of 2.7×10^9 meters per annum. Two additional production lines have been ordered and will be installed to provide a production rate of 8×10^9 meters per year. The new product replaces an older one which consisted of a copper wire surrounded by PVC insulation, a fabric jacket, and a lacquer coating. The new one has a copper wire surrounded by a PVC-TEGDMA* coating which is crosslinked by electron irradiation. This gives it fine electric properties as well as high resistence to the heat of a soldering iron, abrasion, solvents, and flames. The unirradiated formulation is extruded easily and the omission of the lacquer step reduces pollution problems. The product is used in central telephone exchanges where a decrease of almost 70% in packed area is obtained. This saving alone would justify the process. However, even without it, the process is reported to have provided a savings of $ 4 000 000 in the first seven months of its operation.

The large-scale implementation of this radiation process by Western Electric demonstrates that:

1) there are electron beam generators which can operate with a level of reliability comparable to that of plastics extruders;
2) the radiation engineering practice associated with the routine use of the machine is fairly well understood;
3) the cost of electron beam energy is low;
4) the radiation chemistry associated with the use of crosslinking agents provides major reductions in the dose requirements. In addition, the crosslinking agent is responsible for some of the important mechanical properties of the product.

The successful implementation of this process should encourage the management of other industrial companies to treat radiation processing as a reasonable alternative to competitive methods when considerations of cost are favourable. In the past, cost advantage based on the assumption that radiation processing is a routine industrial operation has been a necessary but insufficient condition.

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* Tetraethyleneglycol dimethacrylate

THE FUTURE

In addition to the developments at Western Electric, there are two other phenomena which may have a profound effect on the future of radiation processing: the trend in costs and environmental problems.

The cost of electron beam generators is generally below $ 4 000 per kW and a future cost of $ 2 000 is forseeable. One producer of machines claims electron energy can be produced at a cost of $ 0.25 per kWh; a second producer has estimated costs with current machines as low as $ 0.20 per kWh. Both estimates were for high-powered machines with two-shift operation and a ten-year machine life. Cost estimates by suppliers of accelerators have always been treated with suspicion. This conservative attitude is usually justified but improvements in design and performance have been marching right behind the advancing claims, and they may even be catching up.

ENVIRONMENTAL PROBLEMS

A recent proposal in the U.S. to build a plant for the irradiation of dilute sewage sludge with a dose of 0.1 Mrad to provide E. coli control equivalent to that obtained with chlorination, claimed that an irradiation cost of $ 0.10 per kWh of absorbed beam energy could be achieved. This proposal leads into the use of radiation processing in solving environmental problems. Two types of applications in this category have already been brought to attention: substitution of a non-polluting radiation process for a polluting non-radiation alternative; use of ionizing radiation to destroy pollutants. The first is exemplified by the electron curing of paints as a substitute for thermal curing; the treatment of sewage and industrial wastes is an example of the second.

The use of radiation to treat human wastes has a long but inglorious history. Much of the reported work is poorly done and some of the more extravagant claims are difficult to accept. Suffice it to say, radiation will kill microflora and even (with some difficulty) viruses, but it is difficult to learn what minimum dose level is needed to perform sufficient damage to microscopic life to make the necessary engineering calculations. A pilot scale plant for the irradiation of dilute sludge is now under way near Munich, F.R.G.; hopefully some useful data will be made available.*

The irradiation of plant effluent has been suggested to treat effluents from textile plants to destroy the dissolved dyes. Irradiation renders the dyes colourless under special conditions of pH and oxidant concentration. The same is true for plant effluents bearing traces of phenol or cyanides. One of the more interesting applications proposed in recent years is the irradiation of waste gases from power stations to convert gaseous SO_2 to an aerosol or H_2SO_4 mist which would be trapped in the precipitator. Preliminary results have been very encouraging. The work, now going on at the Takasaki Laboratory of the Japan Atomic Energy Institute and performed in collaboration with the Ebara Industrial Co., is the subject of widespread interest.

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* An International Symposium on "The Use of High-Level Radiation in Waste Treatment – Status and Prospects" is being held in Munich 17-21 March 1975.

Environmental considerations may turn out to be the dominant factor in determining the role to be assumed by ionizing radiation in our industrialized world. The energy required to cure coatings with electrons is 7% of that required with heat. The energy required to sterilize food with electrons or gammas is far less than that required with heat. As the competition for clean fuels increases, the cost of energy may prove to be the dominant cost. A detailed analysis of total energy expenditures is needed to determine whether it will benefit our society to place strong emphasis on energy conservation by widespread substitution of electron beam processes for thermal processes. It is with such a challenge that I finish.

The future looks bright and rewarding. The present isn't too bad, either. It's about time.

The Oklo Phenomenon

by Roger Naudet*

Subject of an International IAEA-Symposium from 23 to 27 June 1975

During 1972, research workers of the French Commissariat à l'Energie Atomique made an astonishing discovery: fission chain reactions had been triggered spontaneously in the very remote past within a uranium deposit in Gabon and parts of the deposit had behaved like a modern nuclear reactor for hundreds of thousands of years. Subsequent investigations showed that the reaction sites had remained in a remarkable state of preservation, so that detailed study was possible.
The IAEA felt that the Oklo phenomenon would be an excellent subject for international co-operation in fundamental research and agreed to the suggestion of the Gabon Government and the French Commissariat à l'Energie Atomique that a jointly organized symposium be held. The symposium will take place at Franceville, Gabon, from 23 to 27 June 1975.

It is a familiar fact that, of the two principal isotopes of uranium, which are naturally radioactive, ^{235}U has a shorter half-life than ^{238}U (7.1×10^8 years as against 4.51×10^9 years). Consequently, the concentration of ^{235}U in natural uranium is decreasing constantly with time; in the very remote past it was much higher than it is now (3.65% two thousand million years ago as against 0.72% now).

A "FOSSILIZED" NUCLEAR REACTOR

It was therefore suggested some time ago that fission chain reactions might have been triggered spontaneously within uranium deposits in the very remote past, given the existence of certain conditions: high concentrations of uranium; the absence of strongly neutron-absorbing elements; and the presence of water. It did not seem out of the question

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