PERSPECTIVE OF RADIATION PROCESSING

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ABSTRACT

The area of the applications of radiation techniques is very wide. This paper only relates to the applications of radiation techniques in industries including radiation chemical industry, radiation processing of foods and environmental protection by radiation, but the nuclear instruments and the instrumentations of radiation are out-side of our study.

INTRODUCTION

The field of applications of radiation techniques is far and wide. They apply in agriculture, medicine, industry, science, etc.. Such in agriculture radiation improves variety of seeds-radiation breeding, radiation promotes the plant growing; in medicine radiation(γ, X, e^-) kiils and wounds cancer cells, doctors diagnose the illness with radiation instrumentations as X-ray therapy, X-CT, etc.; in science the instruments as X-ray photoelectron spectroscope, mass spectroscope, positron annihilation spectrometer, X-ray fluorescent spectrometer, X-ray crystallography, X-ray crystal spectrometer, X-ray diffractometer,......are popularized. All those abovementioned will not be discussed here. This paper is only concerned in the applications of radiation techniques in industries including radiation chemical industry, radiation protection against environmental pollution and radiation processing of foods, and also radiation sterilization and disinfection, whereas nuclear instruments, radiation instrumentations and the applications of radioisotopes are canceled.

A BRIEF REVIEW OF THE PROCESS OF RADIATION PROCESSING DEVELOPMENT

Prior to the fourth decade of the twentieth century the word "RADIATION PROCESSING" had no appeared yet. A few of scientists investigated how the radiation (α, X) initiates chemical reactions in gases and aqueous solutions. No one predicted and expected the radiation to process. In fourth - fifth decades of the century more scientists were fond of investigation in radiation defects of solid substances at first, then started to study how to get the products from radiation chemical processes, as radiation polymerization, radiation syntheses, etc.. It is the stage of dream of the radiation processing. In the late fifties and the sixties more and more scientists were engaged in radiation chemical research, and hoped to produce the products by radiation. At last radiation-crosslinked shrink films in 1957 and radiation-crosslinked polythene wire in 1959 came out. These were the first radiation industrial products in market place. In this period radiation processing from the embryonic stage turned to reality. A dream had come true. In the seventies and the eighties radiation processing developed very quickly not only in U.S.A., Japan and Europe, but also in third world composed of the developing countries in Asia, Africa, Latin America and elsewhere. In developed countries such as in U.S.A. even a radiation processing system shaped up now. However in the People's Republic of China although the scientists started engage in radiation chemistry in middle of the fifties, but due to the all well known cause the radiation processing was very weak yet even in the end of the seventies.

CURRENT STATUS OF THE DEVELOPMENT OF RADIATION PROCESSING

Radiation Chemical Industry

It is concerned here with the new materials synthesized by radiation and raw and processed materials modified by radiation. It includs radiation organic syntheses, radiation polymerization and modification of polymers and certain inorganic compounds. Tables 1 and 2 enumerated the radiation reaction systems which is producing in manufactories or in pilot-plant at present, or has got in prospect of production in the near future.

From Tab. 1 we should indicate some characteristics possessing oneself of radiation syntheses of organic compounds. Radiation synthetic procedures can go on at much lower temperature than corresponding thermal processes. There are no resin-like substances in final products such as in 2,4,8, procedures. Radiation synthetic procedures may much conserve the energy source. For example, using the procedure 7, we can get 200 tons of methylphenyl chlorosilane per year with the aid of a 5 —10 kW electronaccelerator, and get the same annual gross output of pentaphenylsilane with the aid of a 3 —4 kW electronaccelerator. A lot of radiation synthetic processes 2,3',4,8 and 9 has the conversion 90 —100% which means that it will have no any by-product, i.e. will not bring any polluter in production. At last, there is various posibility to produce organic compounds with middle molecular weight whatever you hope by radiation telomerization because monomers may be any alkene and the telomerizing agents may be RX, RCN, RSH, oxygen-containing organic compounds or inorganic compounds such as PCl_3, H_2S, phosphinates etc.. In addition, the price of some radiation synthesized products is much lower than that by thermal processes. For instance the price of branch carbonic acids gotten from ethylene, propylene or butylene and organic acid with C_2 —C_8 by radiation telomerization is only one third compared with the price of that synthesized by thermal processes. And the price of $(Bu)_2SnBr_2$ is cheaper than that produced by Grignard reaction by US$3400 per ton, if annual gross output of $(Bu)_2SnBr_2$ is 200 tons.

Radiation processing in area of polymer radiation chemistry is developed most early, most quickly and most widely as compared with the usage of other areas of radiation chemistry.

There are more than 400 monomers successfully polymerized by radiation in laboratories, but only a few of them realized commercial production as shown in Tab. 2. It would point out that the key of obstacles of extended application of those achievements of radiation polymerization to commercial production is its production cost often higher than conventional one. For the sake of the decrease of the cost of radiation-polymerized products, reduction of the radiation polymerization dose and improvement of the quality of product are most important, except for the decreasing of the cost of radiation and producing superpure polymers using in highfreqency insulation and in biomedicine. Emulsion radiation polymerization merits special attention in this field. Over the late years we successfully accomplished the pilot production of emulsion radiation polymerization for preparation of low temperature binder and thickness for printing on textile with super qualities.

Radiation grafting has various posibility for improving the properties of plastics, films, powder, even textiles, and for obtaining new materials with special properties due to the combination of original properties at least of two components. Radiation grafting in gas phase indicates a pretty future.

The amount of radiation crosslinking products is most in all radiation processing. For example, the value of radiation-crosslinked products of polyalkenes in USA in 1980 achieved 2 billion US dolars, and in Japan in 1979 more than 1000 billion yuans. The gross radiation-industrial output value increases at an average rate of 15-20% per year in late decade. Variety and uses of radiation processed products ard extending very quickly day in and day out. The latest great use of radiation crosslinking appeared in rubber industry. The tyre of today must satisfy the conflicting performance requirements of lower rolling resistance, greater traction and greater treadwear. Radiation processing of the unvulcanized tyre is valuable to us in maximizing each of these performance requirments in the finished vulcanized tyre. Hundreds of million lbs of elastomer were radiation cured by 1985.

Radiation degradation of fibre and cellulose has strongly attracting attention of mankind. Preparation of feed, fuels and chemicals from natural plant(bush, tree, straw, stalks) is equal to greatest usage of solar energy which will bring to mankind greatest benefit. But this radition degradation process needs high absorbed dose, its production cost is too high yet. If any effective way will be seeked to transfer the unchain-reaction to chain process raising the degradation yield G value and decreasing the absorbed dose to the utmost extent, thereby decreasing the cost of products, this process will be extremely useful for obtainment of super fuels and chemicals.

At last, we should indicate the radiation curing process. This process is de-

Table 1. Radiation Syntheses of Organic compounds

No.	Compound	Reaction conditions	G value	%conv.	Production status
1	HCB, etc.	aromatics + Cl_2, γ ambient. temp.	~10^5		was produced, Eng. USSR
2	2-Cl-6(trichloro- methyl) picoline	α-picoline + Cl_2, 120 — 150°C, γ	$4x10^2$	96-98%	pilot production
3	CH_3CHBr	ethylene+ HBr, -2°C, γ	$4x10^4$	100%	400T/yr USA 1970-75
4	1,1-difluorochlo- roethane	fluoroalkylation, 100 — -30°C, γ	10^5–10^6	90%	pilot prod. USSR
5	sulfochloride	$RH+SO_2+Cl_2$, room temp. γ	10^3–10^6		full product'n USSR
6	sulfonic acid	$RH+SO_2+O_2$, γ	10^2–10^3		
7	organosilicons	chlorosilane + RX (Or alkene) 200°C, γ	60–300		10-odd kinds, pilot product'n USSR
8	organooxide	phenol + aromatic ketone, room temp, +37%HCl, γ		100%	
9	$(Bu)_2SnBr_2$	RBr + Sn(powder) γ	10^2–10^4	~100%	200T/yr USSR
10	telomerization	monomer + telomerizing agent, γ	10–10^4		400T/yr tetrachloropentane, each 50T/yr decylchloropentane, $CHCl_2COCl$, CCl_3COCl. USSR

Table 2. Radiation Syntheses and Modification of Polymers

Reaction	No.	Product and properties or usage	Production status
radiation polymerization and copolymerization	1	emulsion polystyrene	was produced USA
	2	polyacrylamide & copolyacrylamide, super absorbent materials	large lot production USA, CN
	3	condensation lens	full production JAP
	4	soft contact glasses	pilot production CN
	5	emulsion copolymers of BA, binder	pilot production CN
	6	emulsion copolymers of acrylate,thickness	pilot production CN
	7	monocrystal of polyacetylenes, nonlinear optical material, semiconductor	
	8	slow release anticancer drug	clinical examine, more than 250 persons JAP
radiation grafting	9	hydroxyacrylamide-polyester-cotton fibre	was produced only 10 year USA
	10	PE (PP)-AA film for food packing	commercial production USA
	11	cation, anion exchanger membrane	pilot production USA,CN
	12	PVC-AN, impactproof, heatresistent	accomplished pilot production USA
	13	PVC-butadiene, improve on impact strength 50 — 100 fold, low-temp. proof	ditto JAP
	14	PE-AA for selective permeable membrane	full production USA,CN
	15	chrome pig leather- MMA or BA, water-proof	
	16	silicon rubber + HEMA + VP + propenol, contact glasses	
	17	clinical polymers	USA, JAP, CN
	18	PTFE-AA, PTFE-ST	USA,JAP
	19	P(TFE-E)-AA, selective absorbent for transition metal ion as U from seawater	JAP

	20	PMMA-sulfurcontaining org. cpd., plexiglass with fine mechanical and flame-retardant	USSR
	21	starch-AN, super water absorbent	pilot production CN
radiation polymerization and radiation grafting	22	composites: WPC	millions m^2/a USA; pilot production Fr, CN
	23	CPC	small lot, USA, USSR
	24	PPC(with $CaCO_3$, M_xO_y, coral powder, gypsum powder, coal ash, mineral ash......)	pilot production
	25	reinforced plastics	commercial product'n USA
	26	metal-plastic composite	under development
	27	silicic acid(ZnO, glass fibre)-VP or St, inorganic-organic exchanger with fine thermal stability	under development
	28	PE-polyester film by surface grafting, packing material	commercial production
radiation crosslinking	29	PE, PP, PVC, Rubber wire and cable	commercial production, USA, UK, JAP, Fr, USSR, Neth, Sweden; pilot prod. CN
	30	SR wire & cable with work at -30—120°C	full prod. JAP, USA, Eur
	31	PVC pipe, transportation of hot water	commercial prod. USA
	32	PE for storage of solar energy	under development
	33	thermal shrinking film, pipe, connector (use of memory effect)	commercial prod. USA, UK JAP, Fr, USSR, Neth, Sweden; pilot prod. CN
	34	trasparent thermal-shrinking film with resistance $4.7 \times 10^{14}\Omega$ at 120°C, fire retard.	under development
	35	foam plastics	commercial prod. UK, USA JAP, Neth. Ital. Austra...
	36	cured rubber	commercial prod. USA, JAP, Fr. USSR
	37	selr-temperature controllable cable	commercial prod. USA pilot prod. CN
	38	NR-PE, St-B rubber-PE, man-made leather	under development
radiation curing (polymerization, grafting and crosslinking)	39	lithography	commercial prod. USA
	40	automobile and bicycle painting	was produced USA, JAP
	41	magnetic memory material	pilot prod. USA, JAP, Eur
	42	nonwoven, antipollute, waterproof and flame-retardant fabrics, flocking	under development
radiation degradation		tailored polymers:	
	43	PTFE, super fine powder with very low friction factor	pilot prod. USA, JAP, CN, USSR, UK......
	44	polythene oxide, thickness, viscosity regulator	commercial prod. USA
	45	butyl rubber, glucosans, PVP as blood infusioner	may be produced whenever nesessary
	46	fibre, cellulose as animal feed, chemicals, fuels	under development, PRB, CN, FRG, USSR, USA

veloped quickly also. According to statistical data, sales of the radiation curing coating in 1973 — 1982 had increased from approximately 1 to 25 million lbs./a. Much effort is being exerted to discover multifunctional monomers especially designed for use in radiation processing in the printing, paper, metal, plastic and flooring industries. Of recent years radiation curing in the manufacture with pilot production of magnetic recording materials (video, audio, and computer tape) came into existence in USA, JAP and Europe. It will bring great economical benefit for industry, especially great social benefit for uses. The reasons for the success of this technology are simple because it is simple, clean and sterile and the producing cost is moderate. It looks as if there will be a lot of so manufactured video, audio, and computer memory tapes in market place for the visible future.

There is only a few of successful radiation processing for inorganic solids. Radiation-treated semiconduct diode switch improves markedly its switch speed. It is producing in commercial-scale in USA and China. Accelerated electron irradiation markedly raises the rigidity of tinplate. The phosphorus-doping into semiconductor-silicon using (n,γ) reaction has been realized. Radiation-coloring of glass, pearls, jewels and gems is under development. I think many things may take place in this field.

Radiation protection Against Environmental Pollution

In harnessing environmental pollution and preserving ecosystem equilibrium radiation chemistry makes beneficial contributions. Besides it has no waste polluting the environment in radiation chemical processing some radiation produced products such as PAAm hydrogel, selective permeable membranes, ionexchangers, could use as cleaner of water, or as preservatives of water and soil. Particularly it is very important that radiation-self could play a significant role in preserving of both the primary natural clean air and water. Table 3 shows the radiation preservation of environment.

Table 3. Radiation Harnessing of Air, Water and Sludge Pollution

Pollution Sources	Toxicant	No.	Treatment	Efficiency
exhaust gases from coal, petroleum or ore combustion	NO_x, SO_2	1	15 kW e^-+ electrostatic precipitator(SO_2 600-900ppm, NO_x 80ppm, 1000 m³/hr, from heavy oil)	removal of 80% SO_2 and ~100% NO_x JAP
		2	e^-+ NH_3 + precipitator (SO_2 200ppm, NO_x 180ppm, from iron ore)	removal of SO_2 and NO_x ⩾90% and 80% respectively JAP
		3	e^- + lime spray(SO_2 1000- 2000ppm)	USA
waste water from chemical plants, printing and dyeing mill, tannery pesticide pollution;	Cl-,CN-containing compounds as polychlorophenyl, phenol, dyestuff. virus, pathogen	4	γ, 10-20 kGy	full decomposed
		5	γ or e^- + chemical treatment or + biochemical treatment such as γ+O_3	tangible result for bioindegradable substances as lignin, formic acid, ethylene glycol, azodye and phenol, special evidence for the decrease of TOC; virus and pathogen are full killed.
sewage treatment plant	10^5/ml microbes	6	Cl_2 + γ, 100—200Gy	markedly decrease the formation of Cl-containing carcinogens
wells	insoluble Fe_xO_y,MnO_2	7	^{60}Co, γ	protection to precipitate. well's lifetime twofoldprolonged GDR
institute of viruses	viruses	8	ditto	fine, cheaper than conventional sterilization Can
sludge	pathogens	9	γ, 4.5×10^5Ci,3.2×10^4gal/d	fine, operated 19 years FRG
	viruses	10	e^-, 4kGy, 8—10×10^4 gal/d	successfully, operated 10 years USA
sewage sludge	ditto	11	100kW 1.5MeV e^-, 1.5m wideth horizontal sewage curtain, 1.5×10^5 gal/d	being operated, commercial system USA
		12	^{60}Co γ 50 t/d	soil conditioner, fertilizer,Can.
dried sludge	ditto	13	^{137}Cs, γ, pilot-plant	fine, soil regulator, feed, USA

sludge cake water-containing 70-80%	coliforms	14	^{60}Co, γ, 0.3-0.7kGy preirradiation, pilot-plant	undetectable level	JAP
garbage human waste	non-endemic diseases	1%	^{60}Co, γ	the cost cheaper than conventional incineration method, Can. airport	

From Tab.3 we come to the conclusion that radiation treatment of air pollution water comtamination and another waste and garbages is effective, beneficial and useful. These technologies are of great importance to mankind, especially to the developing countries. It is very important to make a point that radiation treatment cost of wastes in general is cheaper than the conventional. For example, USA imported technology and equipment of EBA(e^-+NH_3) method from JAP for treatment of exhaust gas, the estimated cost of treatment is cheaper 20% as compared with the conventional one, even the value of the by-product--ammonium sulfateand ammonium nitrate sulfate as fertilizer is not counted in. The USA takes it as a trump card for resolving air and atmosphere pollution. It has predicted that European-American market will reach 6 billion US dollors for installation of EBA technology and equipment from the present up to 2000. However here we should indicate the price is too high yet for the developing countries.

An investigation in this area has not been started truly in China at present.

Radiation Preservation of Food and Radiation Sterilization

Radiation preservation. The most significant items of the beneficial effect of radiation preservation of food are the conservation of energy sources, the reduction of post-harvest losses and the extension of the shelf-life of food, i.e. the increase of food.

Since 1962 a large-scale experiment on food irradiation made in Can. and USA by a mobile ^{60}Co γ-irradiator, various experiments including radiation energy, absorbed dose, repeated irradiation, quality assurance, labelling, microbiological, nutritional and toxicological aspects, and radiation chemistry were engaged in tens countries in North America, South America, Europe, Asia and south Africa. From the results of these experiments, men came to a conclusion: the use of radiation up to a maximum energy level of 10 MeV for electrons and 5 MeV for γ-rays and X-rays is safe and should be permitted for food irradiation; the irradiation of food up to an overall average dose of ten kGy introduces "no special nutritional or microbiological problems"(JECFI, 1980). The number of countries of the international project in the field of food irradiation approaches 30 at present.

The items of irradiated foods recognized internationally by Codex Alimentarius Commission are over 40. According to a rough estimate by AECL, there are ten food irradiation plants in the world, the sum radiation strength 4 million Curies, and annual output 150 kilotons. They are distributed in Canada(2), Belgium(2), France (1),USA and other countries. In China installed an irradiator for irradiation of potatos and fruits in 1985.

The key problems in extended application of the irradiated food are that how much the economical benefit to managers and how to win the acceptance of men of it, and the former is the key to the question.

Radiation Sterilization. Radiation sterilization of medical supplies (such as hypodermic syringes, gloves) and pharmaceuticals is a very established technology in radiation processing in developed countries. Its scale is 2nd for market value in radiation processing. One γ-irradiator for sterilization of medical gloves was installed, another one for sterilization of hypodermic injectors will be installed in China.

DEVELOPING PROSPECTS FOR RADIATION PROCESSING

Radiation processing is an important means in development of material science, an important method for environmental conservation and an effective method for preservation and sterilization. As seen by making a description of above, radiation processing as new technique and technology developed very quickly in the 1970's and early 1980's. It has a bright future although it suffered setbacks in certain processing systems, such as the stop of radiation syntheses of C_2H_5Br and biodegradable detergent, of finishing of polyester-cotton fabric by radiation graft of hydroxyacrylamide, of radiation emulsion polymerization of styrene and of radiation curing of coatings on spares of automobile. But this is a little episode in the advance of radiation processing from general trend of its development. It cann't affect the whole situation of the developing. The reasons are as follows.

1. Ever since the world-wide oil crisis in 1973 traditional overall growth rate of the annual gross output value of radiation processing in average is 15-20% in world. for individual company as Raychem is 25%. This general trend is not reduced in past ten-odd years. The kinds of products, the field and object of processing and the output and its value are increased and extended with high speed.

2. The advantages of radiation processing have a strong attraction for us. They are energy conservation, environmental preservation, nice quality of products, high production efficiency, safety, less workshop field, labour conservation, easier process automation and obtainment of new products unobtainable by other method.

3. Radiation sources are improved gradually. They are adapted for a wide variety of objects. The kinds, stability, safety and reliability of them are increased greatly. Particularly economical electron curtain is developed.

4. The economical benefit of radiation processing is good. The price of radiation energy is acceptable at present. One kW.hr of electron was more expeusive in 1958, and it is ¢25—30 in 1980. Correspondingly for ^{60}Co-γ rays, $10—20 per curie in 1958, and about $1.0/Ci in 1984. The energy consumption in production is smaller, and the cost of expended energy is smaller(see Table 4), thereby the operation expenses are less, and the overall cost of production could be less also.

5. There is the posibility of wide prospects on opening and improving of the radiation processing technique. For example, radiation application maybe extend into the production of inorganic and inorganic-organic compounds; radiation (co)polymerization extends into emulsion and suspension polymerization from block and solution polymerization.

For the reasons as mentioned above, we can undoubtedly say that a beautiful scene of radiation processing will come out in the near future.

SOME PROBLEMS WITH RADIATION PROCESSING DEVELOPMENT IN DEVELOPING COUNTRIES

Both education and technological conditions are key problems with radiation processing development in developing countries. The education is taken aim at eliminating nuclear terror mind for people and at knowing and using radiation technology for them who will be engaged on it. Cheap electronaccelerators with high stability and radiation technology are exactly what developing countries need. If the advanced techniques are grasped by them, radiation processing will develop up to a new level, by then a new epoch in radiation processing will arrive.

Table 4 Comparison of the cost of Energy Consumption Between Radiation Processing With Thermal Processing

Processing object	Thermal processing	Radiation processing	Ratio (therm./radiat.)
PE crosslinking (600V-4/0 wire)	¢ 2.4/kg	¢ 1.1/kg(150kGy)	2.18
curing silica rubber	¢ 6.2/kg	¢ 0.73/kg(100kGy)	8.49
reinforced polyesterplat curing (1500kg/h)	$ 50/kg	$ 12/kg	4.77
paint curing(same flow rate)	$ 9000/month(gas)	$1600/month	5.63
food preservation	¢ 3.7/kg·day(15% load of cold storage plant)	¢ 0.04/kg,once(5kGy)	92.5
medical supplies and pharmaceuticals sterilization	$ 1.80/m³(ETO)	¢ 40/m³(2.5kGyEB)	4.5
thin coating curing*	¢ 65.1/1000ft³(gas stove)	¢ 3.2/1000ft³(Ec)	20.33

* Data are quoted from J. Coated Fabrics, 11, 131(1982), other data are quoted from 3rd IMRP, p.1, Tokyo, 1980.