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RADIATION PROCESSING OF PETROCHEMICALS AND PLASTICS[1]

International Atomic Energy Agency
Vienna Austria

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Interregional Petrochemical Symposium on the
Development of the Petrochemical Industries
in Developing Countries

Baku, USSR, 20 - 31 October 1969

PET. SYMP. C/14

SUMMARY

RADIATION PROCESSING OF PETROCHEMICALS AND PLASTICS

International Atomic Energy Agency
(IAEA)
Vienna, Austria

In petrochemical and plastics industries radiation energy has become a production tool to initiate free radical reactions. The status of radiation processing has been particularly recognized in polymerization, curing and modification of structure of polymers. Cobalt-60 sources of various strength are used to irradiate bulk materials or to induce chemical synthesis. For the continuous processing of thin sheet of plastics or fabrics electron beam accelerators of 0.3 - 3 MeV are very suitable for irradiation purposes.

In the light of current development the following processes are reviewed:

1. Halogenation of hydrocarbons
2. Synthesis of biodegradable detergents

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3. Polymerization of ethylene
4. Solid-state polymerization of trioxane
5. Modification of plastics through cross-linking and grafting
6. Curing of surface coating
7. Wood-plastic combinations and other composite materials
8. Modification of textiles

The merit of ionising radiation is its ability to initiate polymerization in any phase and under mild reaction conditions without the use of catalyst. It is also envisaged that radiation processing will provide new outlets for a variety of monomers through the development of composite materials, surface coatings, modification of textiles and plastics.

The practical aspects of radiation processing are further illustrated by engineering and economic evaluations for some typical processes. It is anticipated that an integrated approach from process development to product evaluation will facilitate the transfer of radiation technology to chemical process industries.

[illegible] used in the [illegible] techniques are [illegible] improve- [illegible] of radio- [illegible] of radiation [illegible] of [illegible] World [illegible] the [illegible] of large rad- [illegible] stimula- [illegible] there [illegible] manufacturing [illegible] of surface [illegible].

[illegible] industrial [illegible]

[illegible]

[illegible]

[illegible] accelerators. [illegible] irradiated. Cobalt-60 [illegible] per curie. [illegible] of dose [illegible] products [illegible] gamma source. [illegible] The merits [illegible] processing are low maintenance, [illegible] and deep penetration [illegible] have been proved [illegible] wood-plastic [illegible] synthesis.

	Co-[illegible]	[illegible]
Half-life, [illegible]	[illegible]	[illegible]
Energy, [illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible] are mainly electron beam [illegible] with energies of [illegible] high dose [illegible] sufficient scanning speeds of electron [illegible] particularly [illegible] the continuous treatment of [illegible] fabrics [illegible]. Figure 1 shows the cost [illegible] types of [illegible].

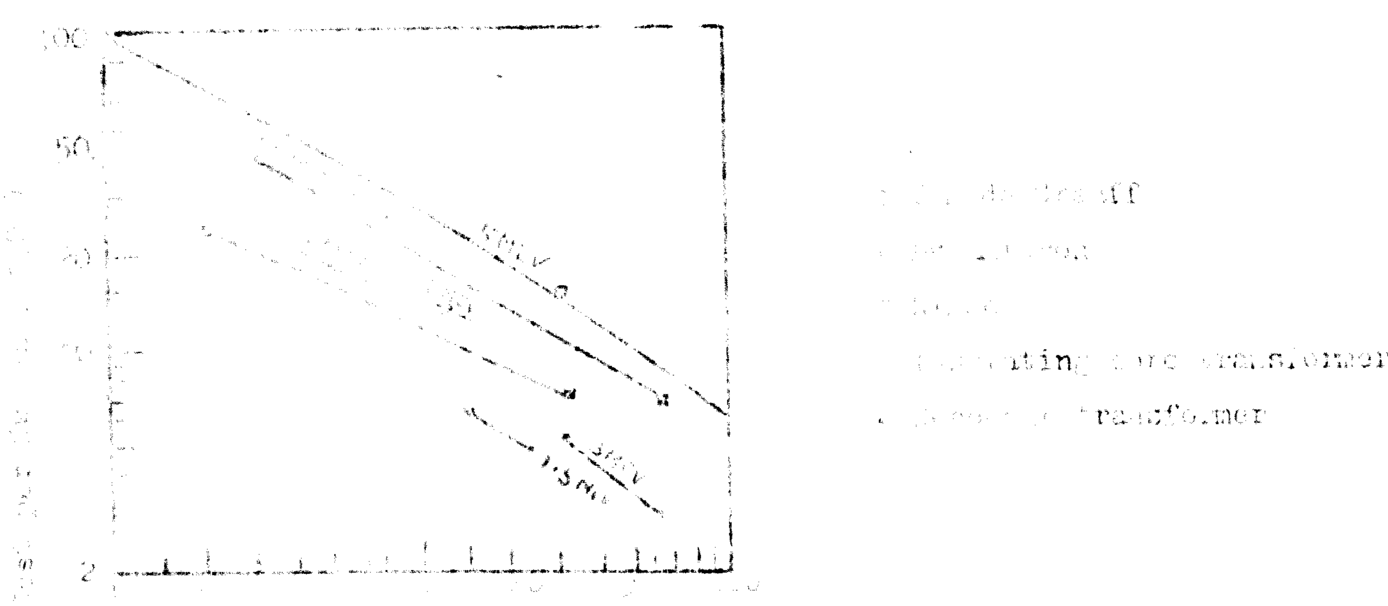


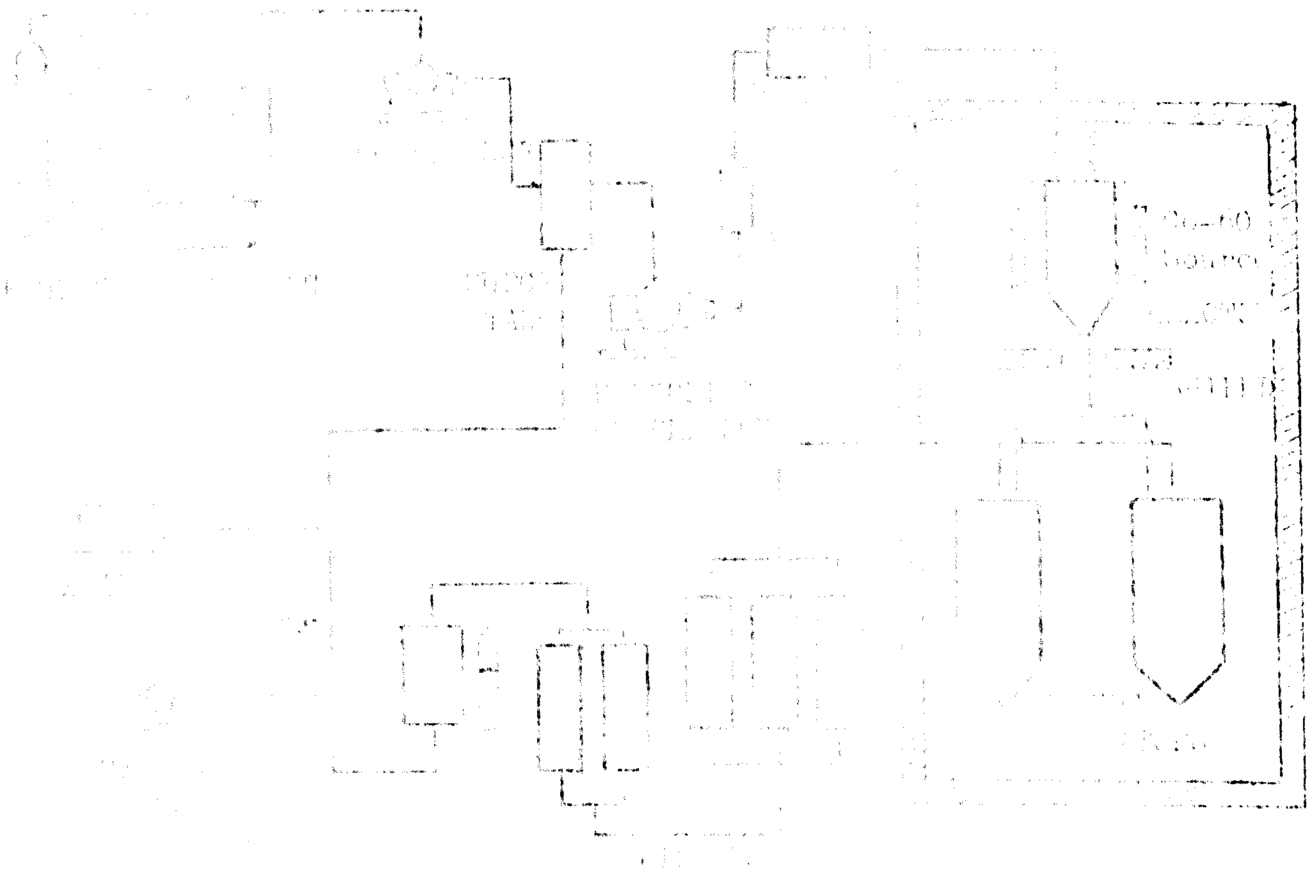
Figure 1. [illegible] Cost of Accelerators

[illegible]

[illegible] polymerization under high pressure has been pursued in the [illegible] of ethylene and its copolymerization with other monomers. [illegible] have been built for process development on polyethylene. Results [illegible] National Laboratory [illegible] process operating below the melting point of polyethylene will yield a polymer of intermediate [illegible] with low melt index, while a low density product with high melt index [illegible] obtained when the operating temperature is above 120°C. At Takasaki [illegible] different combinations to find a solution to [illegible] of polymer [illegible] the wall of reactor (Fig.2). It is [illegible] to facilitate the [illegible] of polymerized materials from the reaction [illegible] the stage where the degree of cross-linking is not excessive. The [illegible] of Brookhaven and Takasaki are summarized below:

	Takasaki	Brookhaven
[illegible]	1. [illegible] autoclave 2. Heated wall	Tubular reactor
[illegible], atm.	440	565-[illegible]10
[illegible], °C	15[illegible]	120-200
[illegible]	[illegible].8	0.35-4.6
[illegible]	Fine powder, sp.gr.=0.94	-
[illegible]	17,[illegible] - [illegible]	-
[illegible]	7.4 - 10[illegible]	5 - 100
[illegible]	115 - [illegible]	-

[illegible] application of the [illegible] process so developed, however, will depend on its com[illegible] technology, which has been [illegible] established and [illegible] for more than twenty years.



[illegible] Polyethylene [illegible]

[illegible] Polymerization of Trioxane

[illegible] is the only [illegible] ing [illegible] anionic [illegible] structures of polymer [illegible] should be expected [illegible] polymerization.

[illegible] trioxane has [illegible] search [illegible] Figure [illegible] shows the [illegible]

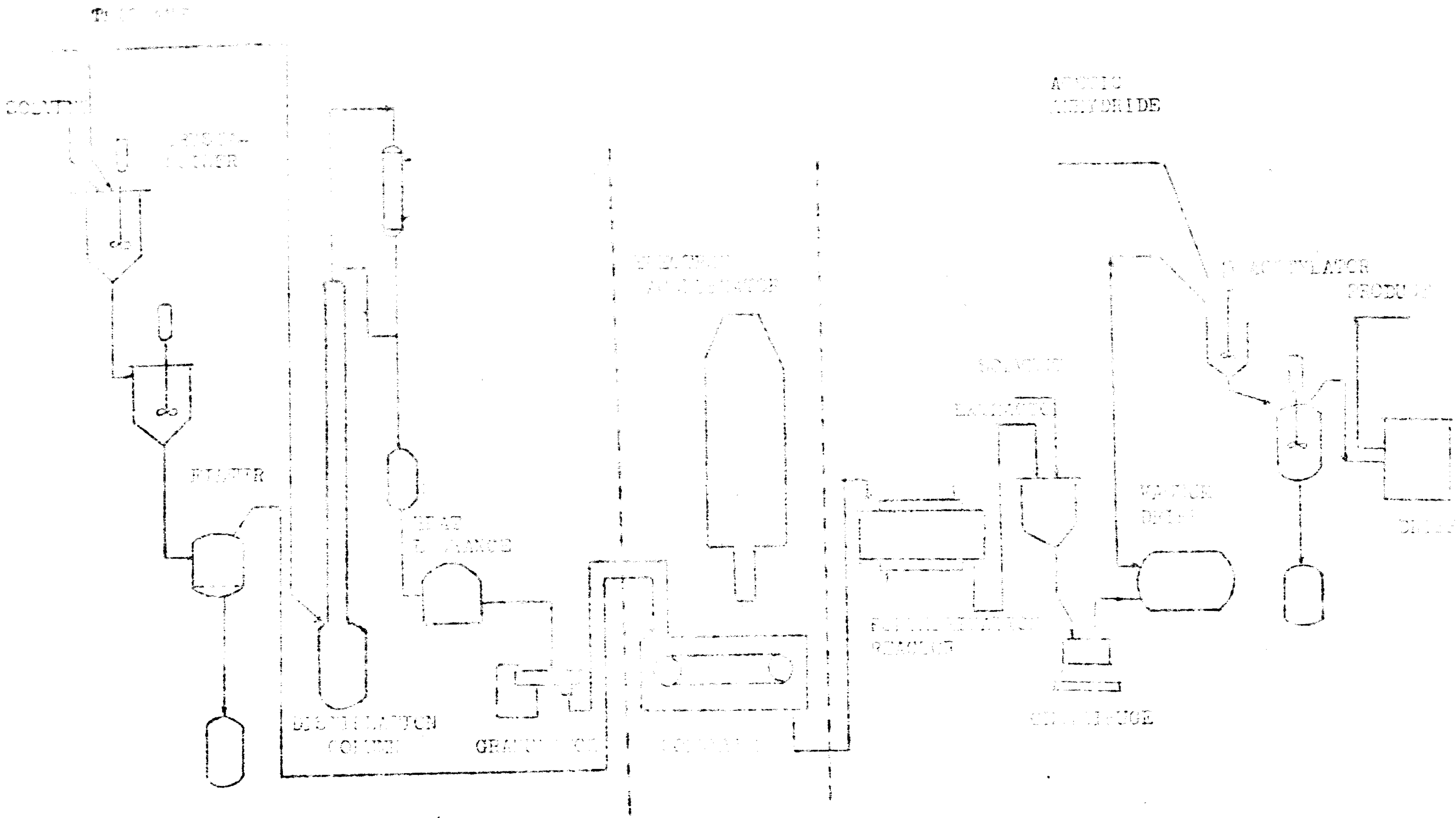


Figure 3. Flowsheet of Takasaki Pilot Plant for Solid-State Polymerization of Trioxane

[illegible] ...lly been [illegible] to free it [illegible] and other impurities. [illegible] of not more [illegible], trioxane was [illegible] electron beam [illegible] type accelerator [illegible] Mrad/sec. [illegible] Polymerization [illegible] trioxane [illegible] at 55°C [illegible] nitrogen [illegible] hours. The polymer was then [illegible] vacuum [illegible] stabilize the polymer [illegible] acetylated [illegible] at 165°C, followed by [illegible] and drying. Table I shows [illegible] mechanical properties of [illegible] polymer produced at Takasaki [illegible].

[illegible] of Mechanical Properties [illegible] by
[illegible] Radiation Process and Commercial Product

[illegible]	Radiation Process	Du Pont 500
[illegible] °C [illegible]	[illegible]	100
[illegible], kg/cm²	[illegible]	700
[illegible]	[illegible]	40
[illegible] ft-lb/in²	[illegible]	2.6
[illegible]	[illegible]	50
[illegible] constant, [illegible] °C, [illegible]	[illegible]	0.02
[illegible] pressure	[illegible]	[illegible]

[illegible] estimated that the [illegible] of the order of [illegible] assuming a [illegible] of [illegible] production [illegible] per year.

<u>[illegible]</u>

1. [illegible]

[illegible] modification of the structure of polymers should be regarded [illegible] commercial application of [illegible]. Crosslinking of [illegible] is usually achieved by post-irradiation of extruded products.

[illegible] initiates the formation of free [illegible] radicals on recombination lead to cross-[illegible] and solvent [illegible] of the polymer.

[illegible] irradiated polyethylene tape [illegible] irradiated polyethylene [illegible] continuous service up [illegible] improved.

[illegible] irradiated polyethylene [illegible] Low or [illegible] tubing, which is squeezed to [illegible] irradiation [illegible] to 2 MeV [illegible] suitable for food-[illegible] polyethylene tubing [illegible] are also entering commercial [illegible]

[illegible] derived from the irradiation of low [illegible] dose [illegible] of a blowing agent.

[illegible] Company in Japan manufacture [illegible] radiation-induced cross-linking of the polymer [illegible]

[illegible] a resilience [illegible] polyethylene [illegible] °C, and can be [illegible] down [illegible] similar technique, [illegible] main advantage of the [illegible] to prevent [illegible] to flow when the [illegible] at elevated temperat[illegible]

[illegible] of 13 Mrad. The use [illegible] or carbon tetrachloride can reduce the dosage [illegible] of [illegible] properties and [illegible] in the vulcanization of thin articles.

ii. [illegible]

The objective of radiation induced graft copolymerization of plastics [illegible] backbone polymers [illegible] grafting can be [illegible] following methods:

1. [illegible] polymer in the presence of [illegible]
2. [illegible] of polymer [illegible] followed [illegible] with monomer [illegible]
3. [illegible] polymer [illegible]

[illegible] number of [illegible] different [illegible] and polyvinyl chloride [illegible] For the [illegible] styrene [illegible] It is [illegible] high [illegible] in such a manner [illegible] of radicals [illegible] monomer molecules.

[illegible] of gaseous butadiene on [illegible] has been [illegible] by the [illegible] Sekisui [illegible] on an inner [illegible] cylindrical vessel [illegible] major [illegible] of impact [illegible] the polymer [illegible] has [illegible] ordinary PVC [illegible] cm[2] [illegible] with butadiene can [illegible] chemical reactivity [illegible]

[illegible] radiochemical grafting [illegible] the preparation of [illegible] membrane [illegible] of cation exchange membranes styrene [illegible] grafted with a few [illegible] of [illegible] polyethylene film and [illegible] sulfonated to obtain [illegible] with high mechanical strength [illegible] The membrane [illegible] electrical resistivity [illegible] less energy in [illegible] in comparison with [illegible] methods. Ion exchange [illegible] prepared by the radiation [illegible] potential applications [illegible] chemical processing and water desalination.

[illegible]

Electron beam curing of unsaturated [illegible] and [illegible] has been on the [illegible] distinctive advantages over conventional prac- [illegible]

[illegible]

[illegible] wide [illegible] could not [illegible]

[illegible]

[illegible] possing [illegible] of the [illegible] cure [illegible] method will [illegible] in applica- [illegible] been [illegible] tack-free [illegible] will eliminate all these [illegible] group [illegible] also [illegible] for marketing. [illegible] process for [illegible] coated [illegible]. Radiation curing [illegible].

[illegible] MeV, [illegible] also possible [illegible] wet-layup laminates, prepregs and even molding [illegible] materials can compete with hot-press cured [illegible] mechanical properties as well as to cost. [illegible] total [illegible] around four [illegible] the devel- [illegible] with [illegible]

[illegible]

[illegible] to wood- [illegible] is [illegible] grafting [illegible] irradiation [illegible] of the [illegible] in this [illegible]

[illegible] France, [illegible] has recently [illegible].

[illegible]

[illegible]	flooring [illegible]
[illegible]	flooring
[illegible]	flooring
[illegible]	[illegible] handles

[illegible] following [illegible] compressive [illegible] In some [illegible] is selected. [illegible] of [illegible] mechanical [illegible]

[illegible], [illegible] better [illegible] resistance. Potential applications can be [illegible] construction, furniture, and sport [illegible]. [illegible] evaluation by the [illegible] it was shown that the [illegible] of [illegible] using TMA [illegible] the price of [illegible] (‛) 0.35/ [illegible]

[illegible] cost is influenced by the selection of [illegible] and operating conditions. The interaction of [illegible] can be shown [illegible]

[illegible] cycle

Mold [illegible] loading [illegible] Monomer

[illegible]

Operating condition

[illegible] | [illegible] transfer | Additives

[illegible] under the same conditions, [illegible] of [illegible] with the type [illegible] most signifi- [illegible] in the following table based on a [illegible] of 25% in the [illegible]

Table III. [illegible] of Processing Cost with Monomer

Monomer	Usage [illegible]	Relative [illegible]	Processing cost [illegible], $			
			Depreciation	Irradiation	Monomer	Total
[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]	0.14
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.1[illegible]
[illegible]	1.0	0.33	0.03	0.07	0.16	0.26

[illegible] should be [illegible] of lower unit cost [illegible] monomer content [illegible]. [illegible] improvement should [illegible] between physical [illegible]. [illegible] homopolymerization and graft poly- [illegible] of grafting on [illegible].

[illegible] quality [illegible] has led to the [illegible] materials. Bagasse board [illegible] successful [illegible] radiation-induced polymeri- [illegible]. [illegible] good dimensional [illegible] mechanical strength. [illegible] some abundant [illegible] fibre [illegible] into useful [illegible]. [illegible] the choice of a [illegible] natural wood price-wise. [illegible] will [illegible] and for [illegible] building material that will [illegible].

[illegible] impregnation and [illegible] materials [illegible] containing [illegible] properties [illegible].

[illegible] Improvements of Concrete Polymer Combination.

Property		% Increase
Compressive strength, psi	20255	285
[illegible], psi	1627	290
[illegible], psi	6.3×10^6	[illegible]
[illegible], psi	2637	[illegible]
[illegible], wt. loss	0.5%	[illegible]

[illegible] will find applications in the field of construction where [illegible] will be encountered.

[illegible]

[illegible] research [illegible] of textiles [illegible] promotes [illegible] to [illegible] comfort

[illegible] onal [illegible] in two [illegible]

[illegible] followed by cross- [illegible]

[illegible] followed [illegible]

[illegible] sets [illegible] drop [illegible]

[illegible] necessary to [illegible] absorption [illegible]

[illegible] functional [illegible] and [illegible] size [illegible] static [illegible] woven [illegible]

crosslinked cellulose

[illegible] commercial production [illegible] very suitable [illegible] megarads per second [illegible] produce fabrics at a speed of [illegible] meters per minute or a [illegible] piece of garment. [illegible] easily integrated [illegible] of the machine being less [illegible] per meter of fabric.

[illegible] processing takes place [illegible] temperature, permits immediate [illegible] reduced [illegible] accompany operations [illegible] temperature is to reduce [illegible] textiles and [illegible] minimum.

Two [illegible] to durable [illegible] are known, one is the [illegible] process and the other [illegible] Carolina [illegible]-Cone Mills process. [illegible] with the addition of [illegible] which helps [illegible] for easier and faster diffusion [illegible] molecules into [illegible].

[illegible] fibres, grafting with a [illegible] monomer system can improve the dye[illegible] and [illegible] static behaviour of the fibres. For instance, monomers such as [illegible]ylpyridine, methacrylic acid [illegible] have been [illegible] fibre and nylon. [illegible] and Hoffman reviewed [illegible] of different fibres, and the trend indi- [illegible] crystallinity of the fibre play a [illegible] polymers [illegible] for better improvement [illegible] low frequency of [illegible] polymers should be avoided as much [illegible]

[illegible]

[illegible] reported the commercial production of ethyl [illegible] of [illegible]. This success meant [illegible] photochemical process. [illegible] is more flexible [illegible] reactions.

[illegible] power [illegible] not limited by the [illegible] effectiveness due to [illegible]

[illegible] for operation or [illegible] to [illegible] of total [illegible]

[illegible] housings will involve [illegible] biological shielding [illegible] effect.

[illegible] ethyl bromide process also featured [illegible] This design [illegible] for chlorination. [illegible] dichloroethane [illegible] production of benzene [illegible] chlorination of [illegible] for [illegible]. At present [illegible] photochemical chlorination.

[illegible] given by [illegible] et al. in the foll-

[illegible] is [illegible] favourable.

[illegible] Operating costs [illegible]
Basis: [illegible],000 tons per [illegible]

	HV Process	Co-60 Process
[illegible]	$ 120,000	$ 67,200
[illegible]	24,000	11,350
[illegible]	3,000	2,000
[illegible]	12,000	6,720
Ope[illegible]	[illegible],2[illegible]	8,600
[illegible]	2,[illegible]	-
[illegible]	[illegible]	-
[illegible]	6,[illegible]	2,400
[illegible]	[illegible]	31,160
[illegible]	$ 26	$ 12.2

[illegible] from report [illegible]

[illegible] Scientific [illegible] Radiation [illegible] production of [illegible] detergents from [illegible] Using a cylindrical [illegible] source the hydrocarbon feed [illegible] and sulphur [illegible] overflow [illegible] and is subsequently [illegible] sulfonates. [illegible] capacity of [illegible]0 kg/hr [illegible] operating cost [illegible] $ [illegible],000.

[illegible] to C_{17} straight chain [illegible] sulphur [illegible] Both Esso Research and [illegible] pilot plant scale. It [illegible] tons of detergent [illegible] required [illegible] of [illegible] 10^5 rad/hr. [illegible] biodegrad[illegible] detergency of the prodnot inferior to that of alkyl aryl sulfonates.

<u>Economics</u>

The fate of any manufacturing process depends on its economic and engineering feasibilities. For pre-investment considerations the following factors constitute the major part of processing cost:

i. Cost of source and its installations

ii. Amortisation

iii. Source replacement

iv. Maintenance

v. Load factor

vi. Production rate from a given output of energy.

Fig. 4 shows the total capital required for investment in radiation sources and auxiliary equipment as a function of radiation output in kilowatts.

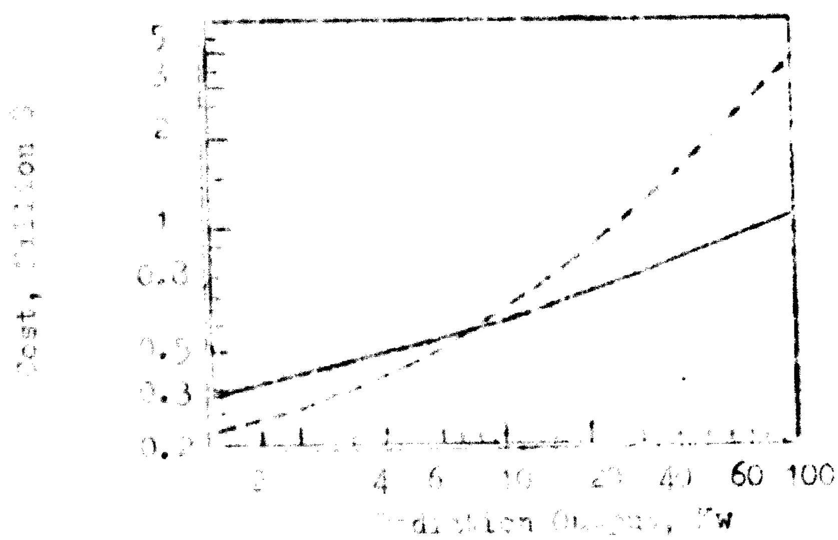


Figure 4. Capital Cost of Radiation Sources

The amortisation of processing equipment varies between 5 to 10 years depending very much on the nature of the process. High depreciation rate is usually considered for processes involving corrosive conditions. Figure 5 shows operating costs relating to source replenishment, maintenance and load [illegible]tors as a function of energy of the source.

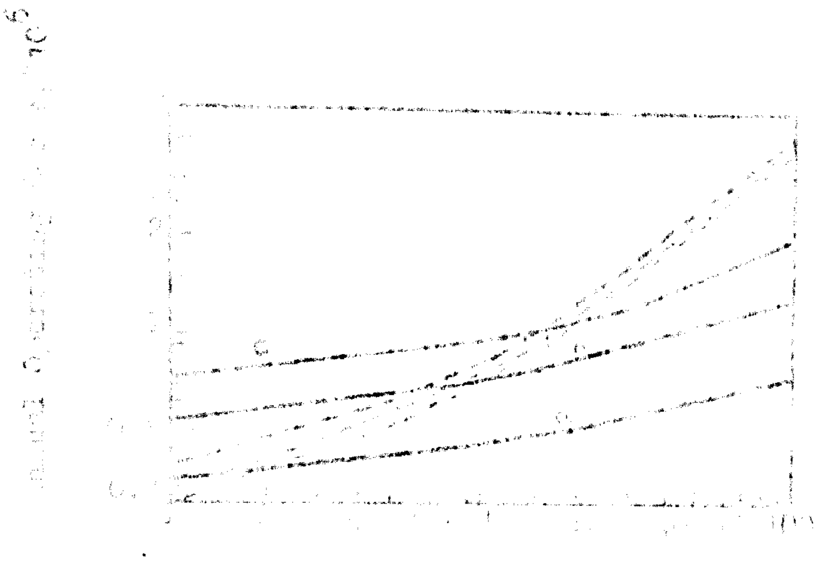


Figure 5. Operating Costs related to Source Replenishment, Maintenance and Load Factors.

The production rate from a given output of energy is directly related to the product of the G-value of energy [illegible] the conversion of 0.0104 [illegible] kilograms of material [illegible] efficiency, where M refers to the molecular weight of the product [illegible] of radicals produced by 100 eV of energy. In polymerization [illegible] it is fortunate to have high G-values in [illegible] chain reactions [illegible] processing. However, the selection of an optimal dose [illegible] process is not determined solely by economic considerations [illegible] almost invariably the processing is exothermic in nature and the rate of [illegible] as influenced by the [illegible] temperature during irradiation [illegible] affects the magnitude of [illegible] selection of dose rate therefore should take into account the coupling [illegible] of these relevant parameters.

The following figures on the various processing costs with accelerators show the relationship of the effect of [illegible] to the economics of processes

[illegible]

[illegible]	Unit	Dose, Mrad	Cost, US cents
[illegible]	[illegible]	5	1
[illegible]	[illegible]	6 - 12	0.10-0.17
	[illegible]	20	0.6-0.9
[illegible]	[illegible]	[illegible]	5
[illegible]	[illegible]	10	3
[illegible]	[illegible]	20	15

[illegible]

[illegible] radiation processing has gained initial successes [illegible] engineering and [illegible] development pro[illegible] [illegible] scale-up [illegible] processes and to lower the [illegible] plant. [illegible] decade ago, the radiation costs were quoted [illegible] and today one can realistically view US$0.5 - 1.0 [illegible] reduction in initial energy cost will facilitate further [illegible] of more applications in consumer products, such as [illegible] increases that radiation can compete with [illegible] use.

[illegible] technology, as in any other technology, [illegible] to bring the concept to process [illegible] successful project always calls for a [illegible] to adopt the technology. As an initial phase of [illegible] development scheme including [illegible] and demonstra[illegible] for subsequent promotion. It is noteworthy to point out that [illegible] research establishments have provided industries with the [illegible] for process evaluation studies and some radiation [illegible] similar arrangement. This will facilitate the [illegible] the process under investigation and also provide [illegible] studies.

[illegible] radiation processing in cross-linking of polyethylene, in [illegible] and in fibrous composites are within the reach of devel[illegible] of the technology to plastics processing and to [illegible] for locally produced monomers will depend on enthusiasm and planning. In such an integrated approach, well-trained engineers and technical people are indispensable. A training programme including radiation chemistry, [illegible], materials testing and product evaluations will be [illegible] feasibility studies which can be organized through demonstration [illegible] plant will clarify the concepts of potential [illegible] and convince the end-users.

15. 3. 72