

RADIATION APPLICATIONS OF PHYSICAL CHEMISTRY

V.L. TALROSE

Institute of Energy Problems of Chemical Physics, USSR Academy of Sciences, Moscow

ABSTRACT. Many chemical energy problems have a physical chemistry nature connected with chemical kinetics and thermodynamics. In our country, the development in this field is associated with the name of N.N. Semenov, who was involved in a large number of fundamental and applied physical chemistry problems. Energy development during the last decades created or sharpened new problems. Our new Institute, the Institute of Energy Problems of Chemical Physics, USSR Academy of Sciences, is dealing with some of them. The present article is an overview of our work on radiation applications. Examples of the use of radiation in the power industry (such as coal gasification), tire production, mechanical joints, metal powder production and sterilization of pharmaceutical products are given. Methods and problems involved in these applications are discussed and the great potential for vast utilization is demonstrated.

INTRODUCTION

The use of energy in technology is ultimately connected with chemical changes of materials. Moreover, mechanical changes as such can be the result of chemical transformations.

Traditional realization of chemical conversions involves reaction in a closed container or in a flow, where the thermodynamics and chemical kinetics influence the process requirements: elevated temperatures for endothermic reactions and quite high temperatures for exothermic processes. The exothermic processes can be conducted in such a way that the heat liberated during the reaction is used to heat-up the reactants, as it occurs in the combustion regime.

The required heat is commonly supplied by contact between a heating media and the reactants including heat and mass transfer. As a result of the energy losses, most chemical industries use heat with an efficiency of only 30 to 60%.

There are many engineering solutions enabling to improve the performance, but none can reach the ideal crushing of solids thermodynamic efficiency. In technologies using mechanical treatment, such as cutting, grinding or crushing of solids, high efficiency is attained by local energy concentration on spines, defect dislocation of solids etc. So, in some cases heat losses are relatively small.

All the cases considered in this lecture are aimed at obtaining new marketable products. The most practical processes, in terms of energy per unit weight, are those in which only a very small part of the chemical bonds have to be converted. For example, by cutting a metal rod to several pieces we break a very small part of the chemical bonds, to obtain a new

useful product. Even if the chemical process consists of only material purification, we also obtain a substance of essentially new consumer qualities.

Changing relatively small number of bonds in a polymer material can be sufficient for an essential change in its thermodynamic and mechanical properties. This is especially true for biopolymers, such as DNA, where the change of only one chemical bond per billion can either be lethal or healing for the cell.

The above considerations ultimately determine objects for engineering applications of different radiation types. In terms of physical chemistry, it is also convenient to differentiate these radiations and relevant treatments into two groups: heating by deep penetration and surface treatment. The first group can involve radiation types and situations in which use of radiation instead of contact heat transfer accelerates the process. Bulk heating by radiation is fast and penetrates relatively deep into the material making it possible to achieve a high uniformity of temperature at various sites or in contrary, to conduct reactions at different rates in various reactor sites. A common example of this method is the use of micro-wave irradiation (MW) in food preparation and many other industrial processes. The effectiveness of MW radiation is due to its ability to penetrate effectively through many dielectrics maintaining sufficient heat transfer per unit volume. It is of interest for relatively large objects. Our multi-year studies show that the MW effect is strictly thermal by its physical nature, rejecting certain mystic concepts in this respect.

Sufficient penetration is also obtained by many kinds of ionized radiation, in particular beams of

megavolt electrons and gamma radiation. Although these kinds of radiation are seldom used as heating agents, they can be applied effectively for heating of reactants, providing the bulk heating required to overtake the chemical process.

The most convincing example of electron beam application as a heating agent is in coal gasification, a purely thermal process. The use of E-beam technology sharply increases the gasification efficiency. Some advantages of this method in comparison to traditional methods of gasification are the elimination of oxygen and the absence of NO_x and SO₂ emissions in the product gases.

The second group, which consists of light, RF and MW, is involved in surface treatment. Pulsed and stationary light, including lasers and discharge of plasmas on condensed substances, is used essentially for very thin layer processes. In general, the practical use of laser chemistry encountered many problems, but that topic is beyond the scope of this report.

Figure 1 gives certain ideas on the penetration ability of various radiation sources in some types of condensed materials (dielectrics, metals). For γ and MW radiation, typical penetration depths are presented, corresponding to exponential attenuation of these types of radiations.

Table 1 presents characteristics of electron accelerators for non-nuclear applications.

The maximum power of a source is comparable with that of common electron accelerators. Gamma power sources are usually significantly lower than the presented values. Nevertheless, they are widely used if there is no need for high energy concentration. Even lower is the emitted power of stationary light and laser sources. A known advantage of lasers is their high beam concentration, which reminds us their application in cutting and point burning.

Table 1. Characteristics of high power electron beams

Characteristics	Range	Typical values
Electron energy (MeV)	0.2-1.0	0.3
Beam current (A)	up to few A	1
Density of energy beam (kW/m ²)	up to 10 ⁸	10 ⁷
Penetration depth:		
gas (m)	up to 10	1
solids and liquids (m)	0.01-0.05	0.01-0.05
Max. unit power (MW)	2-5	0.1-0.5

The power of a single radiation source is always much lower than that of a typical industrial chemical installation or energy equipment in power plants. Hence, a use of radiation sources for large scale applications in chemical industry would be economically unjustified. Radiation technology should be used in processes in which only a small part of chemical bonds (or even only admixtures) is converted, yet ensuring essentially novel consumer qualities. This includes processes involved in the formation of a relatively small, new surface (such as in cutting).

Finally, different problems arise when the system goes through a major chemical conversion due to a small amount of radiation. The most convincing example of this phenomenon is radiation induced chemical chain reactions. However, many chain reactions can be conveniently initiated with no use of radiation.

Consequently, the search for adequate engineering applications of radiation and plasma still remains a very creative task. Specialists know that application of these methods have resulted in products amounting to many billions of dollars, and there is an increasing

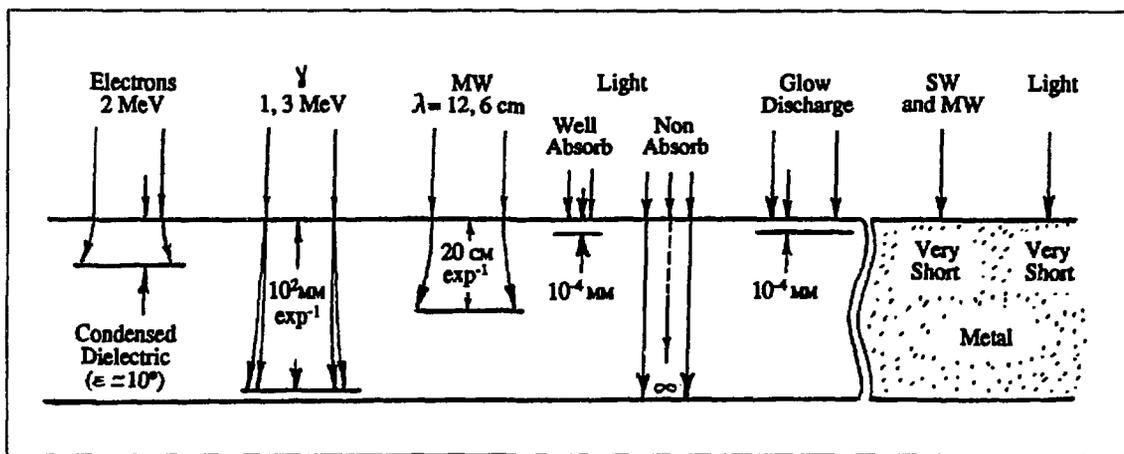


Fig. 1. Penetration ability of different types of radiation

tendency to use radiation and plasma for technological purposes.

Energy considerations in the field of microscopic physical chemistry are discussed next, followed by examples of radiation and plasma utilization.

Ionized radiation and light break chemical bonds mainly due to the Frank-Condon and Born principles, i.e. the so-called "vertical" electron transitions. For instance, the number of chemical bonds broken with fast electrons per 100 eV of the consumed energy varies from 1 to 10 (metals not included). Taking the average of 3 - 4 converted molecules per 100 eV, we obtain a good numerical approximation for prediction of the process energetic efficiency. This seems to be the only example in chemical kinetics, where such accuracy in prediction can be obtained a priori, without experiments. It certainly does not refer to qualitative paths of chemical conversion, which require extensive specific study of individual processes or reaction groups. The above mentioned prediction ability, however, does permit immediate evaluation of the energy efficiency in a radiation chemical process. Since the heat of an individual chemical reaction is usually several eV, thus the efficiency will be only 10 - 20%. This is evidently low and once again shows us that radiation energy must be rationally used. A convincing example of it is the purification of substances from micro-admixtures. The ions, free radicals and excited particles, generated under irradiation of the main mixture component, can selectively attack the micro-admixture, converting it to the desired products. In radiation chemistry this is known as indirect action.

For example, in the case of a dose rate of 50 kGy, i.e. 50 kJ/kg - typical for some practical applications, the conversion of a substance A due to the direct action will appear as:

$$-\Delta [A] / [A]_{dir} < 10^{-2}$$

In indirect action the free radicals generated under irradiation attack solely the micro-admixture A and are often unable to attack the main mixture component. The small admixture "imbibes" nearly all of the absorbed energy, and if its content in the mixture is less than 1, it can be decomposed completely at the dose rate mentioned above.

PURE RADIATION AND THERMO-CHEMICAL RADIATION PROCESSES

1. The clean-up of flue gases

Traditional processes of flue gases clean-up from NO_x and SO_2 involve chemical reactions in a flow, including substances oxidation. The low concentration of impurities ($[\text{NO}_x] = 300\text{-}800 \text{ mg/m}^3$, $[\text{SO}_2] = 1000\text{-}6000 \text{ mg/m}^3$) requires large scale clean-up

installations, high energy consumption, etc. The first large scale radiation oxidation was carried out by Ebara Corp. and Badenwerk AG¹⁻⁶. Ebara attained 95% removal of SO_2 and 80% removal of NO_x for about 18 kGy and the stoichiometric ratio of ammonia. It means that there is a need for an inadmissible number of about one hundred electron accelerators (with power of 100 kW each) to clean effectively flue gases from a typical power plant unit of 200 - 300 MW.

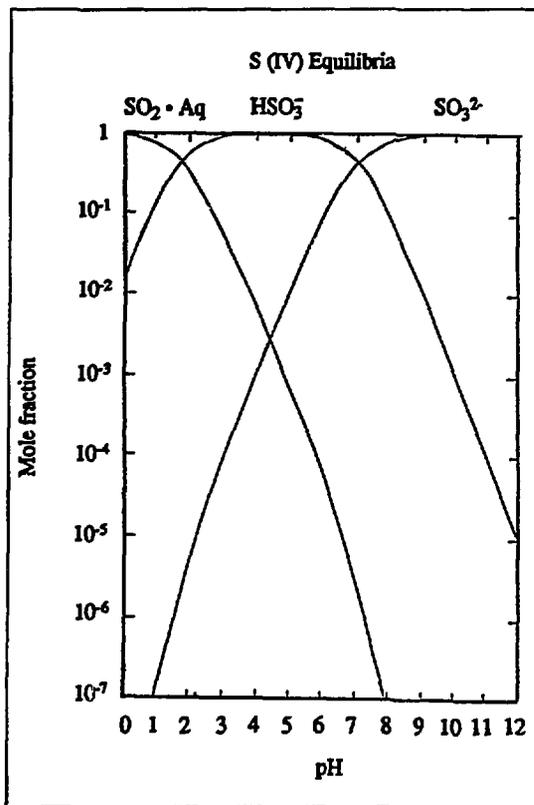
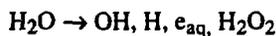


Fig. 2. Sulfur IV fraction in aqueous solutions at different pH

It is well known⁷, that water solutions of SO_2 are not stable and the chain oxidation of SO_2 proceeds at $\text{pH} > 4$. Sulfur dioxide exists in water as three species: hydrated sulfur dioxide, bisulfite and sulfite ions. The fraction of S(IV) in $[\text{SO}_2 \cdot \text{Aq}]$, HSO_3^- and SO_3^{2-} is shown in Fig.2 as a function of pH. Under irradiation,⁸ the initiation of oxidation following water radiolysis may be written as:



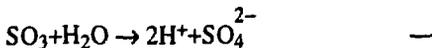
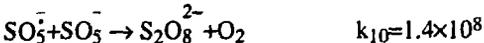
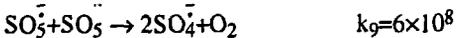
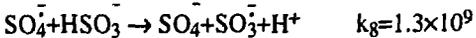
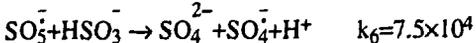
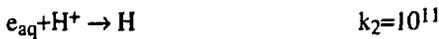
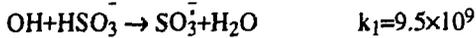
$$G^*(\text{OH}) \approx 3 \text{ (in particles per } 100\text{eV at } \text{pH} < 3)$$

$$G^*(H) \approx 0.6 \text{ (in particles per 100eV at pH < 3)}$$

$$G^*(e_{aq}) \approx 3 \text{ (in particles per 100eV at pH < 3)}$$

$$G^*(H_2O_2) \approx 0.7 \text{ (in particles per 100eV at pH < 3)}$$

where OH, H, e_{aq} and H_2O_2 are the primary components of the irradiated water; G_i is the primary yield for ionized radiation with low linear energy transfer (fast electrons, rays). In acid solutions saturated by oxygen the fate of OH and e_{aq} is:



The rate constants⁹ are given as $M^{-1} s^{-1}$, excluding k_3 , which is given as $M^{-2} s^{-1}$.

The chain length may reach a few thousand per each primary OH radical⁷. The analysis of gaseous admixtures removal by radiation induced chemical reactions in water aerosols indicates that for a liquid phase reaction, the upper limit of droplets radius would not be more than few tens of μm , at a dose rate of a few tens of kGy/s.

Our experiments with water injection into irradiated gas were carried out in a one-pass flow, metal system¹⁰. The experimental parameters were: dose rate of up to few tens of kGy/s; gas capacity of up to $1 m^3/h$; temperature 50-70°C; water content in gas of up to 15% by weight. The concentration of NO_x and SO_2 were measured by a spectroscopic method. The comparison of our data with results of Ebara, and other groups⁵ is shown in Fig.3. It is seen that the

aerosol process proceeds more effectively at doses significantly smaller than the Ebara process. The comparison of our aerosol process and Ebara methods shows that our method requires about one magnitude less power than the others and the number of electron accelerators reduces correspondingly.

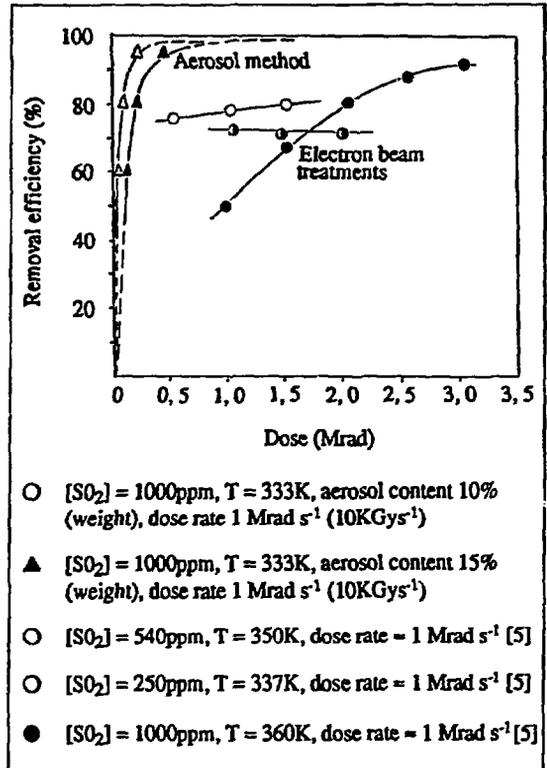
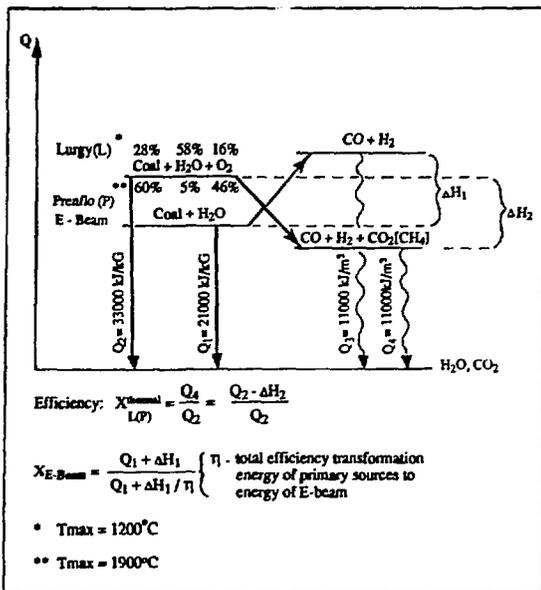


Fig. 3. Flue gas oxidation initiated by the ionizing radiation

The aerosol clean-up process using electron beam treatment will be tested on a large scale at one of Moscow's power plants. The parameters of the installation will be gas capacity of up to ten thousand cubic meters per hour and electron accelerator power of 80 kW. The products of chemical radiation reaction are sulfate and nitrate of ammonia.

2. Coal gasification

Our study¹⁰⁻¹³ showed, that coal gasification is also a pure thermal process. Nevertheless, energy considerations indicate that the radiation method has some advantages over the traditional Lurgi, Texaco, and Shell-Koppers methods of coal gasification. Specifically, the radiation technology has high energy efficiency and specific gasification rate; it also requires no oxygen and is free of NO_x and SO_2 emission¹⁴. A comparison of the E-beam and a



common coal gasification process is shown in Fig. 4. Note that the reagent energy levels shown for both processes do not include energy consumed for oxygen production and E-beam generation. The higher level of coal in the traditional process is due to difference in a heat of combustion. The volume of gas produced per 1kg of converted coal in the E-beam method was higher than in the thermal process. Although the heating value of synthetic gas is close for both processes, the E-beam process leads to a higher energy level of produced synthetic gas.

The design of an experimental facility with two types of E-beam radiation (concentrated and scanning) is presented schematically in Fig.5. Three types of coal were used: brown coal from Kansk-Achinsk, Novomoskovsky coal and charcoal. The coals were not exposed to any preliminary treatment. Particle size was 1-3 mm; moisture and ash contents were about 15 and 5%, respectively^{11,12}.

The steady state rates of hydrogen formation using different coals and accelerator types are shown in Fig. 6. The characteristic feature of these processes is the "threshold" dependency of product formation rate on specific E-beam power input¹¹. The presence of

Fig. 4. The comparison between the electron beam radiation method and the common coal gasification process

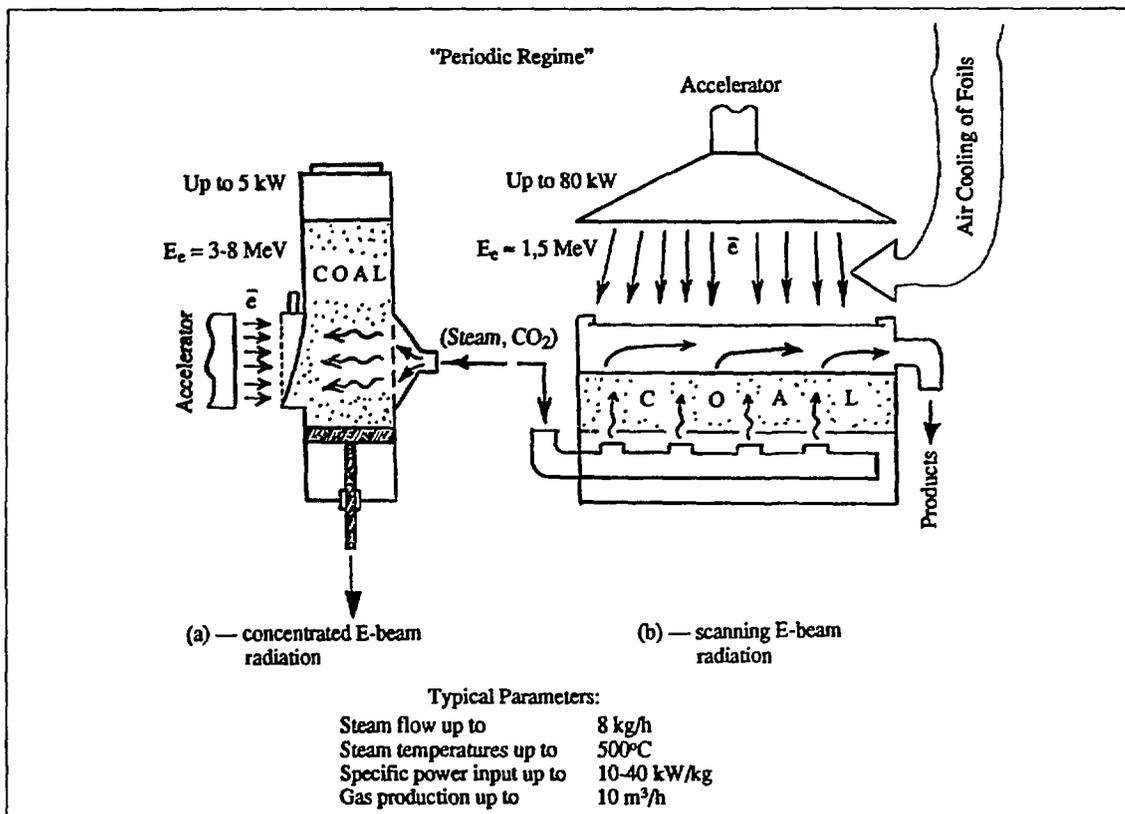


Fig. 5. Schematic presentation of two radiation induced coal gasification processes

"threshold" is explained by the high activation energy (100-150 kJ·mol⁻¹) of coal conversion reactions. The comparison of several gasification parameters is given in Table 2. It is shown that the E-beam process is characterized by a high total efficiency.

To conclude, the E-beam is an energy effective gasification method, well adapted to modern combined cycle. Its further development depends greatly on our ability to design and construct powerful accelerators.

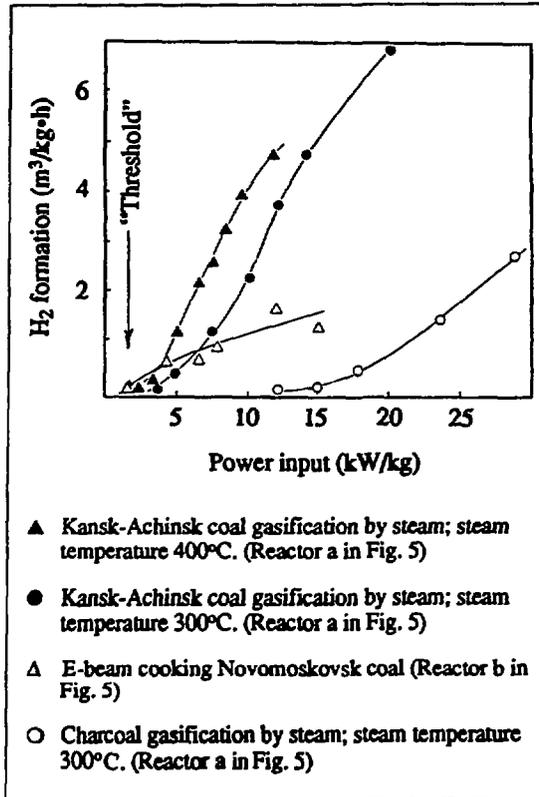


Fig. 6. The rate of hydrogen formation at irradiation of coal
 1 - Charcoal gasification by steam T_s = 300°C;
 2 - Kansk-Achinsk coal gasification, T_s = 300°C;
 3 - Kansk-Achinsk coal gasification, T_s = 400°C;
 4 - E-beam cooking of Novomoskovsky coal

3. Radiation induced chain reaction - CO conversion

The third example of ionized radiation application is the E-beam gas-phase conversion of carbon monoxide by steam¹⁵⁻¹⁶.

The temperature dependency of H₂ chain formation at various H₂O/CO values is shown in Fig. 7, using Arrhenius coordinates. Concentration of CO is growing

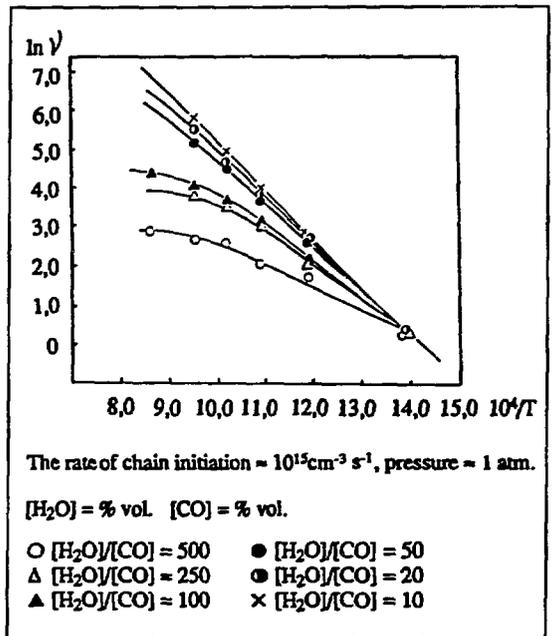


Fig. 7. Radiation induced hydrogen production from gaseous mixtures of H₂ - CO

Table 2. Parameters of coal gasification

Type process	Energy consumption (kWh/kg)	Volume of gas (m ³ /kg coal)	Gas composition (%)	Efficiency (ΔH _{gas} /ΔH _{coal})	Total efficiency of the process
Lurgy, Mark-5	>8 (without energy for O ₂ production)	2	H ₂ , CO (20%) CO ₂ (30%) CH ₄ (10%)	0.7-0.8	0.4-0.5
Shell- Koppers	>9 (without energy for O ₂ production)	2	H ₂ , CO (64%)	0.6-0.8	0.4-0.6
E - beam	5.8 + 3/η*	3	H ₂ , CO (45%)	> 1	0.6-0.65

* efficiency of E - beam generation

from the curve 1 to the curve 6, where it is equal to 10% of the volume. The rate of chain initiation is about $10^{15} \text{ cm}^{-3} \text{ s}^{-1}$. The highest chain length, reached at T_{max} , is about 500. It is possible to produce 1000 m³ of hydrogen per hour by using a 100 kW commercial electron accelerator.

As a conclusion, the efficiency of radiation induced chain reaction can be proven theoretically by the following approach. Two main areas should be founded, as it is illustrated in Fig. 8. In the first one, above curve 1 (high I and low T), the rate of radiation initiation is much greater than the rate of thermal initiation (radiation induced chemical reaction); in the second one (high T and low I) the rates of a thermal initiation exceed the radiation-chemical one. The region below curve 2 corresponds to a reaction with a chain length greater than 2. The region below curve 3 corresponds to conditions where the overall reaction rate is sufficiently high. Curve 4 corresponds to a dose rate which could be created by a high power E-beam accelerator. Only in the region bounded by ABCD we have radiation induced chain reactions with a significant chain length.

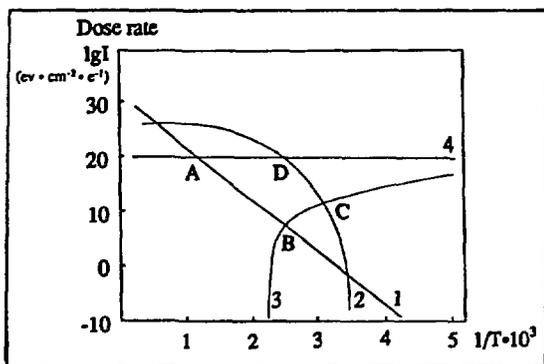


Fig. 8. The area of radiation induced significant chain reactions

SURFACE MODIFICATION OF ELASTOMERS BY LOW TEMPERATURE NON-EQUILIBRIUM PLASMA TREATMENT

Elastomers are used as seals in a number of devices and machines; they have significant adhesion to many materials including metals. Consequently, the opening of an elastomer seal is often difficult after prolonged operation in static conditions.

Serious difficulties arise also when elastomers are used in dynamic connection seals, both for rotational and reciprocating motions (the friction coefficient for an elastomer-metal bond has a value of 1.5-2.5). As a result, the movement produces great power losses, heating and wear of the friction pair. Some seal designs

have been suggested, in which low friction coefficient was achieved due to an especially shaped rigid teflon seal, containing a coil spring which provides elasticity. We offered an alternative approach to this complex and expensive technology. Our method is to utilize the plasma chemical coating of common rubber articles by a thin "teflon-like" polymer layer. This technique reduces the friction coefficient for an elastomer-metal pair, by an order of magnitude¹⁸⁻²⁵. A typical joint is shown in Fig.9. Fabrication of such coating comprises exposure of the elastomer surface to the plasma in the presence of fluoro-containing compounds. The plasma reactor²¹ includes a system of discharging electrodes operating at 50 Hz. The item placed in the reactor is rotated, so that every part of the surface is exposed to the plasma for nearly the same period of time. The coating process mechanism is as follows: UV radiation from the plasma and its electrons which are at a temperature of several eV, induce the formation of active gas particles and free valences on the elastomer surface; interaction between gas particles and the surface interaction results in the formation of the desired one micron thick layer on the elastomer surface. This layer was found to have an "island" structure with narrow straits between large "islands". This process is applied in our country on the industrial level. The industrial reactors have a volume ranging from one liter up to several m³. The modified seals are used in watch seals, turbo-generator shafts and other engineering applications. The seals were found to be especially helpful in compressors of oil pipe-lines.

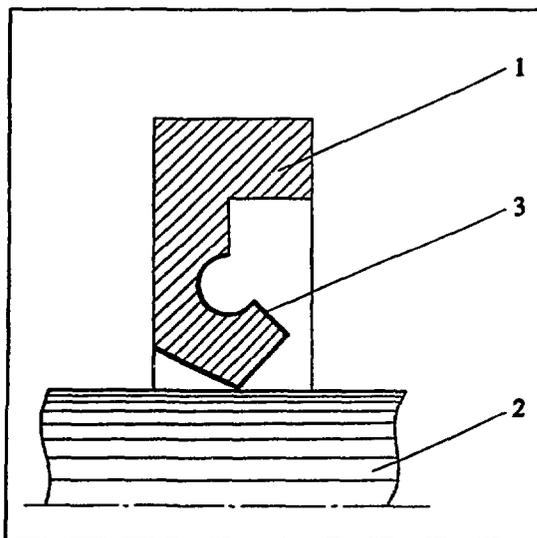


Fig. 9. A typical elastomer - metal dynamic seal
 1 - elastomer part;
 2 - metal shaft;
 3 - fluoro-containing layer

Energy consumption for the surface modification is about 0.1 kWh per 1 kg of elastomer. Utilization of the seals in the long oil pipe-lines of the USSR saved over the last 5 years about 120 million rubles (in prices of 1989).

MICROWAVE TECHNOLOGY

An example of microwave (MW) application is the microwave heating in vulcanization of tires²⁶⁻²⁷. Studies of microwaves transmittance through pure and filled elastomers were carried out to implement this technology. It was found that the e-fold attenuation reaches about 20 cm inside the tire material at 12.6 cm wave length. It was this frequency which was chosen in designing the equipment. Microwave application accelerates the process of tire preheating and heating inside the vulcanizer. This shortens the production cycle by one third. In addition, the tires have better quality and their wear resistance increases due to more uniform heating during vulcanization.

Fig. 10 shows the apparatus for fast preheating of tires. Fig.11 represents the diagram of a vulcanizer with partial heating by microwave energy.

RADIO FREQUENCY HEATING

Radiation at an intermediate frequency (440 kHz) is used for smart technology of metal powders production²⁸⁻³⁴. The wavelength used is the same as that needed for surface hardening of metals. Schematic view of a high frequency inductor for metal powder production is shown in Fig.12. A high frequency inductor (1) heats the end of a wire and a molten metal droplet is formed at this end. The droplet is held hanging in an electromagnetic field. The field keeps the droplet in place, permitting fast downward movement of a carrier gas containing condensed vapor, which is synchronized with the mechanical wire movement; the powder is collected on the filter (3) and then shaken into a powder container (4). If an inert gas is the carrier in a flow recirculation system, the vapor purifies the gas and the final powder is then extremely pure (note that we don't use any crucible). If two or three-component alloy is required, the droplets are fed by two or three wires.

When an oxide metal compound is desired, we add to the gas the necessary reactant (e.g. oxygen). Different sizes of powder particles can be produced by changing pressure, power, and flow velocity. The possible particles size ranges from hundreds to thousands of angstrom.

Electron microscope superscript of silver particles with an average size of 1500 Å is shown in Fig.13; a similar picture of 700 Å nickel particles is shown in Fig.14; here, the particles are aligned by magnetic force.

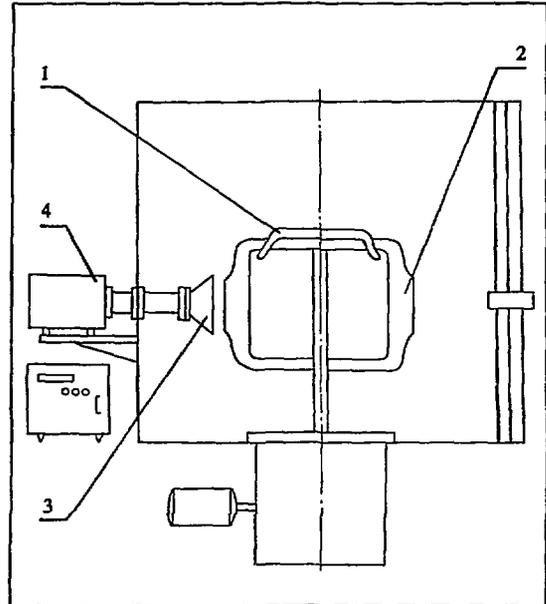


Fig. 10. A prototype apparatus for fast MW preheating of raw tires

1 - holder; 2 - raw tire; 3 - microwave radiator; 4 - generator

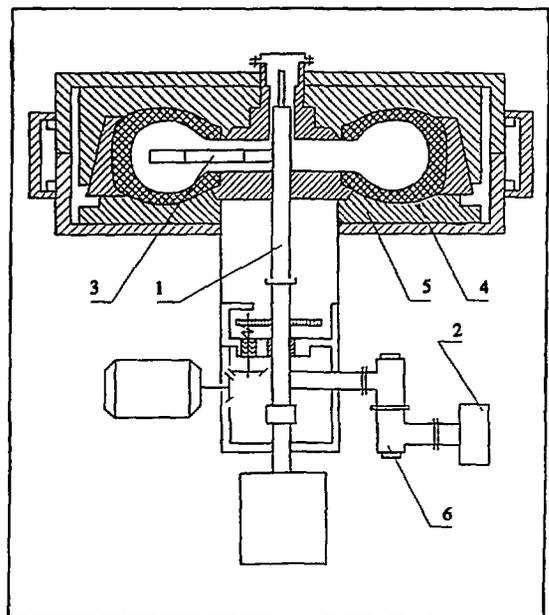


Fig. 11. A prototype of vulcanizer with partial MW heating of tires

1 - round wave guide; 2 - generator; 3 - MW radiator; 4 - tire; 5 - vulcanizer chamber; 6 - power transmitting line

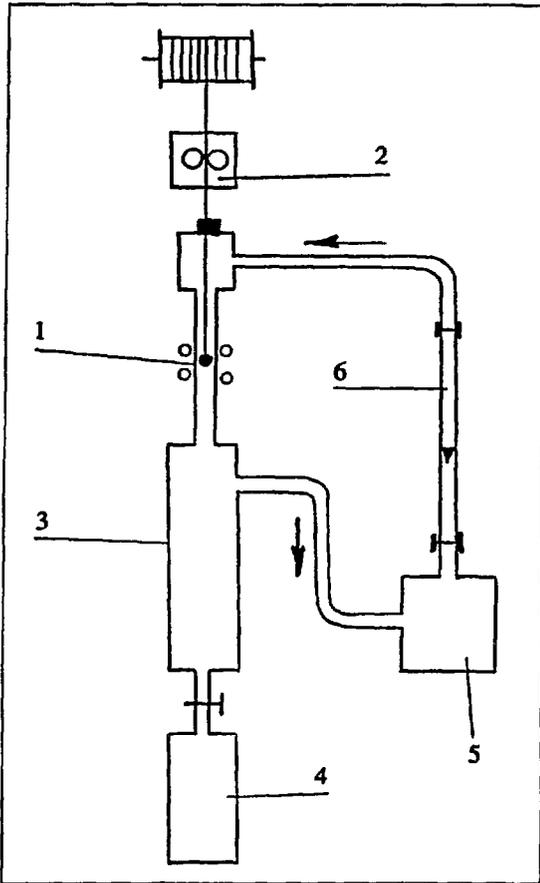


Fig. 12. High-frequency inductor for metal powder production with a levitating droplet method
 1-metal droplet, surrounded by induction heater; 2-wire guide;
 3-filter; 4-powder collector; 5-ventilator; 6-recirculating line

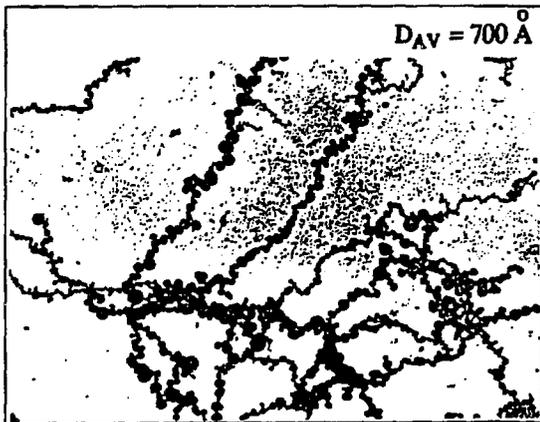


Fig. 14. Electron microscope picture of nickel particles aligned by magnetic force

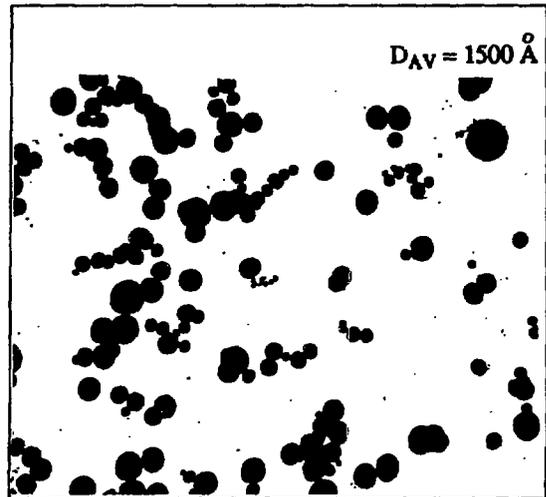


Fig. 13. Electron microscope picture of silver aerosol particles

The mathematical theory of the process is quite complicated. Comparison of the experimental size distribution of the silver particles with that predicted by the theory is shown in Fig. 15; the agreement is quite satisfactory. This size distribution is narrow enough for many applications.

Table 3 gives a list of metals, alloys and oxides whose powder processing technology is ready. If necessary, the method can be used to produce powder of many substances.

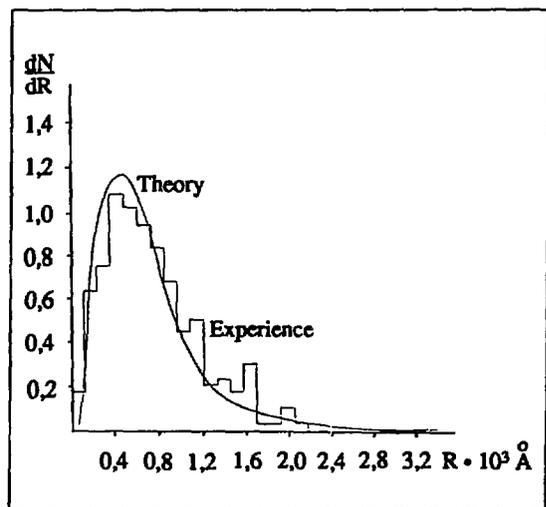


Fig. 15. Comparison of theoretical and experimental size distribution of Ag aerosol particles

Table 3. List of ultrafine metal powders produced by radio frequency heating

Powder type	Average particles size (in Å)	Powder type	Average particles size (in Å)
metals		alloys	
Ag	1000-2000	Fe - Al	500-2000
Al	1200-3000	Fe - Co	160-900
Bi	1200	Fe - Ni	300-900
Co	100-900	Fe - Cu	350-1200
Cu	300-1500	Fe - Gd	1000
Fe	100-900	Ni - Al	700-1200
In	no data	Ni - Co	160-900
Mg	no data	Ni - Cu	400-1000
Mn	no data	Ag - Al	2000
Ni	160-850	Ag - Cu	500-1300
Pb	3000-5000	Pb - Sn	1000-3000
Sn	300-1000	Cu - Sn	no data
Ti	200	Co - Fe - Ni	300-900
Zn	1000	Fe - Ni - V	300-900
Gd	1000	oxides	
Cd	no data	CoO	500
intermetallic alloys		NiO	500
NiAl	700-1200	CuO	700
AgAl	2000	ZnO	no data
Ni ₃ Al	500-900	SnO ₂	no data
		NiFe ₂ O ₄	no data
		γ - Al ₂ O ₃	500-1500
		γ - Fe ₂ O ₃	500

RADIATION STERILIZATION

The last example of radiation applications is sterilization, which is used in biotechnology, pharmacology and medicine. From the chemical kinetics point of view, E-beam and gamma sterilizations of drugs are similar to radiation clean-up of fuel gases. Our Institute is therefore working in this field as well.

Fig. 16 demonstrates schematically the requirements for a sterilization process of a system which is comprised of microorganisms capable of multiplication (including viruses). Two parallel processes take place in any sterilization treatment,

namely inactivation of microorganisms (two lower curves in Fig. 16) and destruction of a sterilization substance (presented by the upper curve), which can reduce the compound's usefulness³⁵⁻³⁷. Therefore, the objective is to find an appropriate sterilization method and optimize its operation to give a reliable inactivation of microorganisms, while the system's functional properties do not change beyond a permissible level.

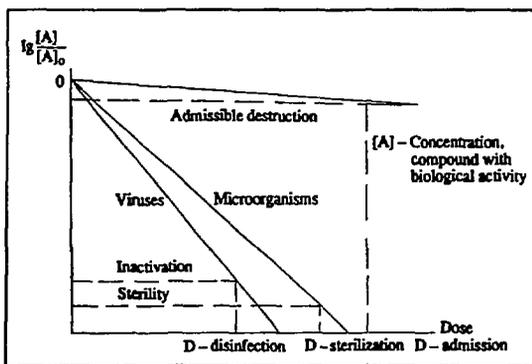


Fig. 16. Schematic demonstration of sterilization requirements

Such optimization can be described by the same idea of a competition between direct and indirect actions which were used earlier. The irradiation doses required to sterilize some complex labile drugs (injections, solutions, sera, vaccines etc.) are near 25 kGy. In the case of a direct radiation effect, the decomposed part of any substance is approximately proportional to the number of chemical bonds in the molecule, and hence to the molecular mass M_a . For relatively small molecules ($M_a = 100-1000$), typical for many drugs, the decomposition would not exceed one percent of the drug which we have to protect during sterilization at the mentioned dose quantity. Note, that the DNA molecular mass of microorganisms can be 10^6-10^{10} Daltons. Radiation sterilization would therefore reduce their population by 10-15 or more when exposed to doses of 10-50 kGy. This is the main reason why radiation sterilization of drugs is possible, while the process cannot be applied to larger molecules.

In most systems that undergo sterilization (mainly water solutions) direct irradiation dominates, while supported by indirect radiation action of free hydroxyl, for instance, which attacks drug molecules. In diluted water solutions indirect radiation at a dose of 10-50 kGy leads to the complete destruction of the substance we have to protect during sterilization. This led to the development of methods which could eliminate the indirect irradiation action. One way is a freezing of the drug solution before irradiation; it is possible to freeze

the water and the drug separately³⁸⁻⁴¹. Figure 17 shows that in a typical case - radiation sterilization of vitamin B₁₂ in liquid water solution its complex decomposition takes place at a dose of less than 10 kGy. On the other hand B₁₂ is stable in a frozen solution, when exposed to doses exceeding those necessary for sterilization⁴²⁻⁴⁵.

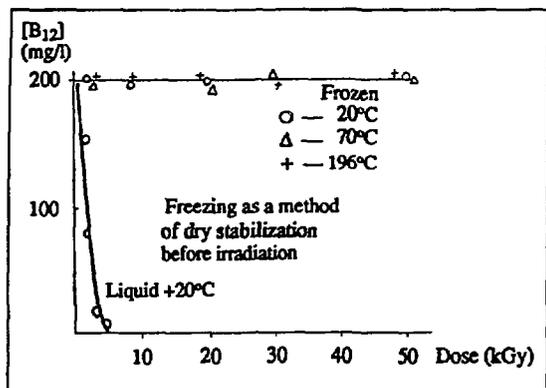


Fig. 17. Radiation sterilization of vitamin B₁₂ water solution

This method was successfully applied also to solution and suspension forms of insulin (Fig.18), making it possible to develop a technique for safe sterilization of any insulin form⁴⁶⁻⁴⁹.

Figure 19 shows that liquid state radiation sterilization of influenza viruses suspension activates safely both viruses and exogenic microflora, but at disinfection and sterilization doses the vaccine activity decreases. In contrast, programmed freezing stabilizes viral proteins to such an extent that the sterile vaccine maintains its biological activity (Fig.20). This means that even proteins with a mass of about 100,000-200,000 can be rather stable in frozen solutions under conditions of radiation sterilization.

Similar results have recently been obtained for other protein systems, including those of blood. It might be possible to use the method for deactivation of viruses which can be transferred via donor materials (hepatitis, HIV etc.).

Another method we use for a similar purpose is the application of UV-light. Fig. 21 demonstrates how microbic contamination grows on tablets which are covered layer by layer by contaminated material (flour, sugar,etc.)

We have developed a special kind of equipment which enables us to achieve two aims simultaneously: to produce coatings and to treat coated tablets with UV-light (which leads to decontamination level similar to that of sterilized tablets). The application consumes only 10kJ/kg of the drug, (the lower curve in Fig.21).

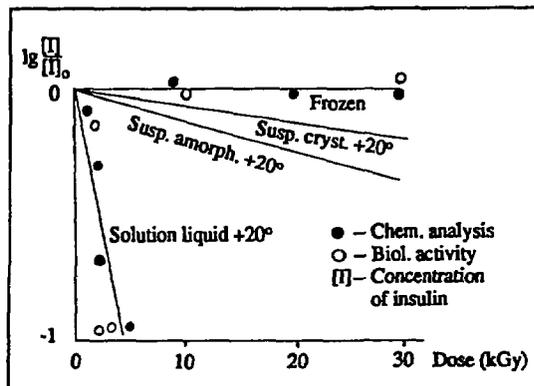


Fig. 18. Radiation sterilization of insulin

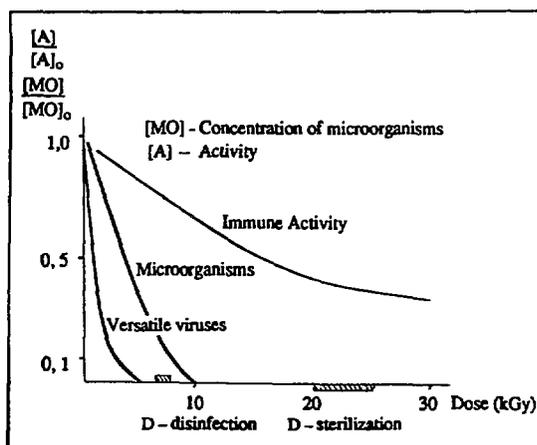


Fig. 19. Radiation sterilization of liquid influenza vaccine

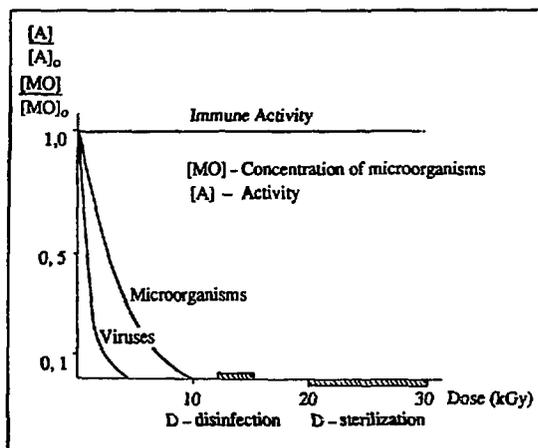


Fig. 20. Radiation sterilization of frozen influenza vaccine

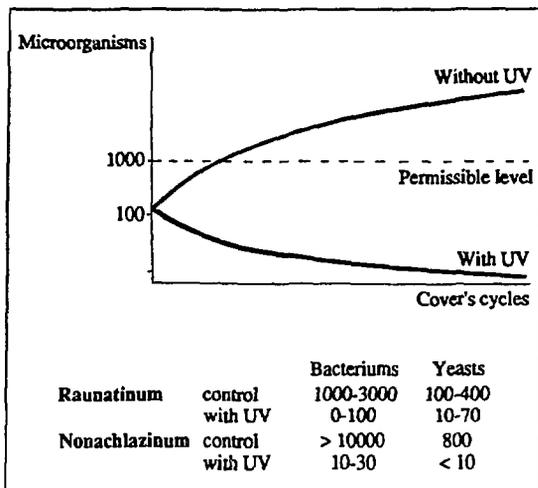


Fig. 21. Microbial contamination of covered tablets

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