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THE HISTORY OF INTRODUCING THE SILICONES IN POLAND

HISTORIA WPROWADZENIA SILIKONÓW W POLSCE

Summary: The present elaboration presents a fragment of the history of developing and implementation of the manufacturing technology and application of silicones in Poland. At present, the silicones are already well known in Poland not only for plumbers or producers of windows, restorers of monuments and physicians but also for the users of cosmetics or baby pacifiers. Market-oriented economy and prices decide on the choice of the supplier. Undertaking the studies and a small-scale production about 70 years ago has contributed to their wide utilization and benefits for the economy.

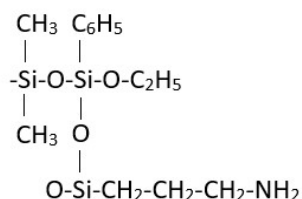
Keywords: silicon, oil, fluid, rubber, resin, hydrolytic poly-condensation, monomer polymerization

Streszczenie: Artykuł przedstawia fragment historii opracowań i wdrożeń technologii produkcji oraz zastosowań silikonów w Polsce. Obecnie silikonów są już dobrze znane w Polsce, nie tylko hydraulikom czy producentom okien, konserwatorom zabytków i lekarzom, ale też użytkownikom kosmetyków czy smoczków. Wolny rynek i ceny decydują o wyborze dostawcy. Podjęcie przed blisko 70. laty badań, niewielkiej produkcji przyczyniły się do ich o szerokiego wykorzystania i korzyści dla gospodarki.

Słowa kluczowe: silikon, olej, kauczuk, żywica, polikondensacja hydrolytyczna, polimeryzacja monomerów

What are the silicones?

Silicones are organic polysiloxanes – high molecular silicon-organic compounds, composed of silicon atoms, linked with oxygen bridges, similarly as in non-organic silicates, but containing, additionally, organic groups, connected with the silicon atoms, such as, for example:



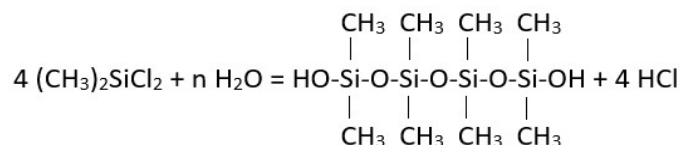
We can distinguish three varieties of silicones: oils (fluids), rubbers and resins. Oils have a structure of simple or branched siloxane chains with a molecular weight in the range of several – few thousand g/mol. Rubbers – elastomers have the structure of long siloxane chains with the molecular weight from few thousand to several hundred thousand g/mol. Resins have the structure of siloxane networks with the molecular weight amounting to few hundred – several thousand g/mol.

From the mentioned three basic varieties, the new type of silicones such as emulsions, pastes, greases, gums, glues, fitters, varnishes, paints, hydrophobic, antifoaming and anti-adhesive agents and others, have been developed and are still produced.

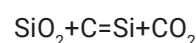
From among plastics, the silicones are distinguished by the following specific properties:

- thermal and oxidative resistance in a wide spectrum of temperatures from -60°C to 250°C,
- the resistance to the effect of atmospheric factors, UV radiation and other,
- good dielectric properties,
- hydrophobic capabilities,
- a small variation of physical properties in a wide temperature spectrum.

Silicones are mainly obtained in the processes of hydrolytic poly-condensation or polymerisation of monomers, as e.g.:



Methyl- and phenylchlorosilanes and their derivatives: alkox-, acetoxy- and vinylsilanes are most frequently used monomers but many reactive organic compounds are employed, as well. The most important raw material, used in synthesis of monomers is metallic silicon, non-occurring in a natural form, but synthesized in metallurgical processes from silicate and carbon in the following reaction:



The first trials to synthesize organic polysiloxanes at a laboratory scale were conducted in the thirties of the 20th c., mainly in the reaction of silicon tetrachloride with the magnesium-organic compounds and then, hydrolytic polycondensation of the obtained magnesium-organic compounds. The attempts to utilize the mentioned method in production of silicones were undertaken at the beginning of the forties by General Electric and Corning Glass in the USA, as performed by the teams, guided by W. Patnode and E.G. Rochow. After certain time, E.G. Rochow invented more economic method of direct synthesis of methylchlorosilanes in reaction of powdered metallic silicon with methyl chloride, with the participation of copper powder as a catalyst. The reaction occurred at the temperature of 260-300°C in fluidal phase, in the special reactors. There was obtained a liquid mixture of the products which were separated by a fractionated distillation method in the columns with a very high efficiency. Four methylchlorosilanes were separated: CH_3SiCl_3 , $(\text{CH}_3)_2\text{SiCl}_2$, $\text{CH}_3\text{SiHCl}_2$ and $(\text{CH}_3)_3\text{SiCl}$. There was always developed the method for synthesis of phenylchlorosilicones in reaction of powdered silicon with chlorobenzene at temperature of ca. 450°C, also with copper or silver catalyst.

Production of the silicones started in 1943 in the USA, and in the fifties, it was also commenced in Great Britain, France and Federal Republic of Germany, on American licences and, also, on the own developments, in the Soviet Union and Democratic Republic of Germany. In the Eastern Europe, the work on the production technology of monomers and certain varieties of the silicones was conducted at the mentioned time – apart from the Soviet Union and DDR – at the Academy of Sciences in Prague. The first American publications, patents and the first monographs appeared: American – by E.G. Rochow, – Russian by K.A. Andrianov and Czech – by Prof. Bažant and Chvalovski; the recent one was translated into Polish in 1955 [1].

The beginning of the research studies in Poland

In 1952, the Ministry of Chemical Industry instructed the former Institute of Plastic Materials (ITS) in Warsaw to develop the technology of synthesizing the silicones, including varnish resins for production of heat-resisting silicone paint, necessary for painting the nozzles of military aeroplanes MIG on the Soviet licence. There was created a team, consisting of several persons, guided by L. Zakrzewski. The author of the present paper received a task to develop the synthesis of methylchlorosilanes.

After having familiarized with the available abstracts in *Chemical Abstracts* and assembling the appropriate apparatus, we brought the samples of ferrosilicon with Si content equal to 90–95%, and the samples of copper powder and methyl chloride. After grinding the ferrosilicon and collecting the sieved powder with grains below 0.1 mm, we conducted the trials to synthesize methylchlorosilanes in pipe reactors, heated in electric furnaces at temperature of 260-320°C, passing the methyl chloride vapours over the mixture of silica with the addition of copper and collecting the condensed mixture of methylchlorosilanes which were separated by a fractionated distillation [2, 3, 4, 5]. After con-

ducting ca. 150 trials during ten months, which lasted 100 h each of them, we commenced (in 1954) the trials of synthesis at a semi-technical scale in a metal reactor, containing 50 kg of silicon and equipped with the agitator and electric heating system. The obtained methylchlorosilanes were separated on a glass column with 50 mm diameter and height of ca. 6 m, filled with glass helices, with the electronically operated head.

In parallel, the team of scientists conducted the studies on synthesis of phenylsilicone monomers in reaction of silicon tetrachloride and bromobenzene by Grignard method and later on, the attempts to synthesize silicone oils and resins from the obtained monomers. They commenced a series of publications on silicones and their applications [6,7,8,9,10] while conducting the consultations with the representatives of western companies, which offered the samples of the silicones and the prospects. In 1958, the author of the present paper participated in the conference on silicoorganic compounds held in Leningrad and delivered a lecture concerning Polish trials to synthesize methylchlorosilanes [11].

I developed the monograph concerning the applications of silicones which was published in 1964 [12]. We got information on the studies on siliconorganic chemistry, as being conducted in the fifties by the teams of Z. Lasocki at the Łódź University of Technology and of W. Rodziewicz at the Gdańsk University of Technology. When possessing the above information, we organized symposium of the experts in siliconorganic matters at our Institute (in 1965). During the mentioned seminar, the research achievements and the possibilities of cooperation as well as financing of the studies were discussed. When perceiving the visible benefits resulting from such meetings, the participants of the conference agreed to organize the symposia of Polish “siliconorganic chemists” every three years. During the next meetings, the successive teams joined the debates; their number was increased, inter alia, by the scientists from the University of Poznań, Gdańsk Medical University and the Centre of Molecular and Macromolecular Studies in Łódź.

Preparations to production

As we could not continue production of methylchlorosilanes at the Institute (threat to the environment), we obtained – in 1958 – a decision of the Ministry of Chemical Industry on the transfer of further semi-technical trials and construction of technical installation to the Chemical Works in Nowa Sarzyna. In 1962, there was created a small Department of Silicones at the mentioned plant. It was equipped with the reactor for synthesis of methylchlorosilanes, transported from our Institute. The installation for their fractionated distillation and some sets of the equipment for semi-technical production of silicone fluids and resins were assembled. Production of methylchlorosilanes (with my participation) was commenced and the first attempts to synthesize silicone oils and resins were carried out.

Manufacturing capacity of monomers did not exceed 3t/year what was insufficient quantity for a profitable production of the silicones. In 1964, the Chemical Works did not have the

sufficient financial means for the project and building of technical installation and eventual purchase of licence, so they gave up the continuation of production and transmitted the mentioned object to the Institute. It became transformed into Experimental Station of Silicones (Polish: ZDS) which was subordinate to the management of the Institute. We utilized the new possibilities of importing the monomers from the Soviet Union, and later on, from DDR and we introduced practically the technologies of synthesising different varieties of silicones for the successive 30 years. The mentioned silicones were developed at our Institute in a laboratory scale. We cooperated with the employees of the Experimental Station in the field of the production improvement and in marketing.

The beginnings were very difficult as it was a period of the so-called cold war and the heavy and military industries were mainly financed at the cost of chemical industry, including industry of plastic materials, and the research work. There was a system of limited distribution of foreign currency for import of raw materials and equipment for possible investments. In the sixties and the seventies, there were considerable restrictions in contacts with the western scientists and companies and the passports for common citizens were practically unavailable.

Apart from introduction and development of the successive varieties of the silicones, the important task of ZDS included the development of the methods for attestation and then, technical conditions and elaboration of the prospects and guidelines to be employed as well as claims of 15 trade names at the Patent Office. After overcoming the synthesis of methylchlorosilanes, we were occupied in development of the successive production technologies of silicones and the attempts of their introduction; it was carried out at the Experimental Station (ZDS).

Methylsilicone oils

The first silicone oils, as developed at the Institute in the period of 1954–1956 by M. Tomaszewicz [13] were methylsilicone oils; they were obtained by the hydrolysis of dimethyldichlorosilane with water and after the separation from hydrochloric acid, by condensation of the resulting dimethylsiloxanols with hexamethyldisiloxane ("MM") which served for termination of dimethylsiloxane chain. The length of the resulting siloxane chain and the relating viscosity of the oil were regulated by the choice of the quantity of the added MM.

After implementation of the described above technology at the Experimental Plant in 1964, there were introduced oils, named "*Silol*"; they had five viscosity values in the range of 20–1000 MPa·s. We developed also the method for obtaining water emulsions of the mentioned oils. In 1965, we introduced four emulsions *Aquasil* to manufacture.

The successive products, obtained from methylsilicone oils and colloidal silicate and introduced at ZDS were two silicone pastes – "*Silpasta*". We utilized methyl dichlorosilane $\text{CH}_3\text{SiHCl}_2$, obtained during the synthesis of methylchlorosilanes, and dimethyldichlorosilane and we developed the method for synthesis of methyl hydrogen silicone oils [14, 15, 16]. The

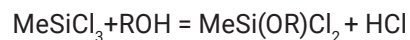
mentioned method was later employed in obtaining of the agents for waterproof impregnation of fabric – *Siltex*.

In 1973, the management of Chemical Works Sarzyna made the contacts with the French company Rhone-Poulenc; within the frames of the mentioned cooperation, there was undertaken production of methylsilicone oils, water emulsions and pastes produced from semi-products, imported from France. The Department of Silicones was organized in the Chemical Works and in 1975, it commenced a technical-scale production of methylsilicone oils and their processing into emulsions and pastes; their semi-technical production in the Experimental Station was stopped.

Methylsilicone resins

The first methylsilicone resin was obtained in 1955 at the Institute of Plastic Materials (ITS). It was carried out by dropping methyltrichlorosilane to water, separation of solid resin from hydrochloric acid by filtration and washing out with water. Then, the powdered resin was dissolved at hot in a ca. 40-% solution of potassium or sodium hydroxide. The obtained solutions of methyl sodium and potassium silicates were used (after appropriate dilution with water, most frequently to 5%) as the agents for hydrophobicity of different materials (it will be described later on in the present paper).

Potassium methylsilicate, called *Ahydrosil-K*, was implemented at the semi-technical scale in 1965, in the Experimental Station. Our main task was however, to develop varnish methyl silicone resin for manufacture of heat-resistant paint. The attempts to synthesize the mentioned resin were conducted by hydrolytic polycondensation of methyltrichlorosilane with a small (up to 10%) addition of dimethyl dichlorosilane, in the solutions of various solvents, using water with the addition of different alcohols. Owing to the application of alcohol, we were successful in mediating the process of polycondensation of monomers; apart from hydrolysis of Si–Cl bonds at the border of organic phase and water, the alcoholysis in organic phase had place in the solution of monomers of the most reactive Si–Cl bonds in methyl trichlorosilane:



After many trials, we chose toluene as solvent and cyclohexanol with a very limited (ca. 3%) water-solubility as a moderator of hydrolysis; owing to this fact, in spite of a small addition of dimethylchlorosilane (up to the methyl groups content, expressed by ratio of 1.09 mole of CH_3 per 1 mole of Si), the cyclohexyl groups – OC_6H_{11} were additionally built-in the structure of resin. Their quantity was – according to the results of elementary analysis and NMR – equal to 0.08–0.13%. Moreover, thanks to the better solubility of cyclohexanol in toluene than in water, its losses in the process of water phase separation and washing of the obtained resin solution were limited. In effect of conducting many trials, we established the recipe and the method for synthesis of varnish methylsilicone resin and we applied for the patent rights for the

mentioned method. We prepared also the respective publications [17, 18, 19]. In 1964, the discussed above resin was introduced to a semi-technical production under the name *Silak M10* at the Experimental Station.

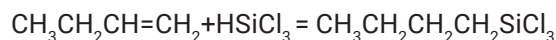
In the years 1962–1965 we carried out also the trials to synthesize methylphenyl- silicone resins, utilizing dimethyldichlorosilane, methyltrichlorosilane and phenyltrichlorosilane as monomers. Toluene or xylene, usually at the 50-% concentration was used as solvent. The mentioned above monomers were mixed at various concentrations and we conducted their hydrolysis, using water with the addition of butanol or cyclohexanol, at the temperature of 15–20°C [20]. After separation of the lower phase of acid and washing out with water, the obtained solutions of siloxanes were subjected to polycondensation by heating up in thermostat and mixture with the addition of 10-% alcohol solution of KOH as catalyst. The described process was controlled by the increase of viscosity and interrupted after reaching the defined viscosity, by the neutralization with alcohol solution of HCl [21].

The properties of the obtained varnish films were examined by pouring the steel sheets with the toluene solutions of resins. Then, we tested the time of drying at temperature of 150°C and time of hardening at 250°C. We measured the thickness of the obtained films, their hardness and resistance to bending as well as dielectric properties. We observed also their thermal resistance when heating the coatings at temperature of 250°C. We developed seven varieties of methyl phenyl silicone resins [22, 23, 24]. All the resins has a good heat resistance and adhesion to metals (excluding copper, its alloys and zinc) as well as wood and minerals but a different flexibility and rate of hardening. They were introduced to production at ZDS gradually with the demand in the period of 1969–1975.

After having found the suitability of our methylsilicone resin – *Silak M10*, the industry of paints and lacquers informed about a big demand on these products what caused the necessity of assembling a separate technical installation. As we had neither means nor the place in the ZDS in the discussed period, we adopted the offer of the Chemical Works (in 1975) which possessed the non-utilized object at that time. After assembling the necessary installation at the capacity of ca.300 t/year, the manufacture of modified methylsilicone resins, named *Silak M101* was commenced. The described object was attached to the Department of Silicones in the Chemical Works.

The necessity to employ the solvents was a certain shortcoming of our resins in comparison to e.g. polyester and alkyd resins, used in the industry of paints and varnishes. We tried to seek the possibilities of obtaining more “organic” resins, i.e. not containing the solvents; therefore, we undertook in our Institute of Industrial Chemistry – IChP (orygenized from ITS) in cooperation with the team of B.Marciniak from the Poznań University – the attempt– to synthesize butylchlorosilanes and to apply these monomers in obtaining the liquid, non-solvent containing silicone resins. We utilized trichlorosilane HSiCl_3 , produced at the Nitrogen Plant in Tarnów and butylenes from the Petrochemical Works in Płock and we conducted the trials to synthesize butyl-

chlorosilanes by addition of technical butylene (mixture of n-butene and iso-butene) to trichlorosilane, with the use of platinum catalyst in reaction, e.g.:



We tested also the possibilities of synthesizing butylmethyldichlorosilane when replacing trichlorosilane by methyl dichlorosilane $\text{CH}_3\text{SiHCl}_2$. The conducted reactions consisted in passing the gaseous butylene through the heated solutions of chlorosilanes with the addition of catalyst and cooling down the products and then, separation and purification of the obtained n-butyl and iso-butyl monomers by distillation [25]. After elaboration of the method and performing some trials at the semi-technical scale, we utilized the obtained butylsilane monomers for development of the synthesis of few varieties of butylmethyl-, butylphenyl- and butylmethylphenyl silicone resins [26]. According to the expectations, the obtained series of the new resins, with a lower content of solvents, and of the solvent-free ones was characterized by a good miscibility with varnish alkyd and polyester resins, at a smaller hardness as compared to methylphenylsilicone resins [27]. The samples of several varieties of the new resins were forwarded to Manufacturing Plant of Paints and Varnishes in Radom with the aim to try them; we offered also the mentioned products to Włocławek Factory but they were not interested in undertaking the task of elaborating newer paints, having better thermal resistance and other properties but being undoubtedly more expensive. It was also connected with undertaking marketing activity. Also, The Tarnowskie Works stopped producing trichlorosilane at the discussed period.

In 1997, we commenced the trials aiming at synthesis of methylphenylvinyl silicone resins by the method, proven in synthesis of methylphenyl silicone resins. We utilized there vinyltrichlorosilane, produced at the Unisil Enterprise in Tarnów. We developed the synthesis of few varieties of resins, differing in composition and properties [28]. The mentioned resins, as containing vinyl substituent capable of copolymerization, were utilized at our Institute in development of the method for emulsion copolymerisation with butyl acrylate, methyl acrylate, vinyl acetate or styrene. The copolymerization was catalyzed by peroxides. There were developed various siliconorganic dispersions for obtaining the paints; they were covered with the patent rights and published [29, 30].

In the years 1989–1990, we utilized the obtained methylphenylvinylsilicone resins and we were successful in their quick cross-linking after addition of polymethylhydroxysiloxane and platinum catalyst at temperature of 80–100°C. We obtained transparent soft gels with the dielectric and mechanical properties, favourable for electronics [31]. The mentioned resins were employed in the preparation of two-component fillings for microelectronic devices. They were successfully tested at the Tele and Radio Research Institute, Centre of Semiconductors - “Unifra CEMI” and at the National Institute of Telecommunications in Warsaw. The aim was to protect the semiconductor structures on the printed circuits, with the application of dropping dosim-

eters. I had the pleasure to submit our achievements in this respect during the conference in Edinburgh in 1990 [32].

In the years 2009–2010, we conducted the trails aiming at obtaining the solvent-free silicone resins, containing substituents capable of cross-linking via polymerization with the participation of peroxides. The mentioned experiments were conducted in cooperation with the research laboratory at the “Polish Silicones” Plant in Nowa Sarzyna (established in 2000, from Experimental Station and Department of Silicones in Chemical Plant)). We synthesized resins, containing additionally – apart from methyl and phenyl groups – vinyl and metacryloxypropyl groups, capable of polymerisation. They are obtained in two typical reactions: 1. hydrolytical polycondensation of solvent solution organochloro- and organoalkoxy-silanes and 2. thermal and catalytic polycondensation of polyorganosiloxanols. The obtained several ten types of resins did not contain solvents and created polymers after addition of peroxide at temperature of 100-120°C during some tens of seconds. [33].

Silicone rubbers

When conducting the trials of obtaining the oils with viscosities above 1000 MPa·s, we commenced (in 1967) the synthesis of liquid methylsilicone cross-linking rubbers without heating and of two-component tuber pastes [34]. There were developed the methods for synthesis of elastomers with the viscosities from few to several thousand MPa·s, with the chains terminated with silanol groups (-OH). The methods of their cross-linking, with the utilization of different metal-organic compounds and their grinding with silica and other minerals and pigment with the aim to obtain paste were tested and improved. The mentioned processes were carried out without heating, receiving the gums with a required consistency and destination. After improvement of the methods for preparation and choice of the first recipes at the Institute, the further work was conducted by the employees of the Experimental Station.

There were conducted the varieties of elastomers as fillers and sealants for electronic purposes as well as varieties of pastes for gypsum forms for moulding of different products made of wax, paraffin, epoxy or polyester resins, or of gypsum. The Experimental Station (ZDS) developed the production of the mentioned rubbers quite quickly; the discussed materials found many users. In parallel, J. Maciejewski and his team worked at the Institute in the synthesis of methylvinylsilicone rubbers with higher molecular weight [35] and on the cross-linking putties, as affected by the air humidity. The varieties of methylsilicone rubbers, containing acetoxyl groups and cross-linking due to the humidity in the air were introduced in the nineties at ZDS in a new building, after assembling the line for packing into containers. They were mainly applied as hydraulic sealant putties. High molecular methylvinylsilicone rubbers were implemented as late as in 2003, on the Chinese licence at “Polish Silicones” Plant which was established in 2002. The manufacture of the mentioned rubbers was commenced at the scale of ca. 400 per year. In the successive years, there were assembled the respective installations in the mentioned plant and the processing of the discussed rub-

bers into silicone gums was undertaken. It commenced the new stage of development of silicones what exceeded the frames of my paper about the beginnings of production and application of silicones in Poland.

Auxiliary silicone aids

Hydrophobic agents

Many varieties of silicones reveal hydrophobic properties what was utilized in a different way, e.g. in hydrophobization of surface or in water-resistant impregnation. We utilized methylsilicone and methylhydrosilicone oils and methylsilicone resins and we developed the products in a form of oil and resin solutions in volatile solvents or in a form of water solutions for sprinkling, pouring or coating with paint. We developed also various agents for waterproof impregnation of building materials, different porous materials, fabric, etc. Potassium methylsiliconate *Ahydro-sil K*, as described above was a cheap and universally applied agent, especially used in construction industry. Silicone compositions, employed in hydrophobization of radio-technical ceramics were also successful and improved dielectric properties [36]. A lot of work was dedicated to elaboration and implementation trials of silicone agents for impregnation of textiles (*Siltex*). The mentioned processes were carried out at the Department of Silicones in the Chemical Works in Sarzyna and will be discussed later on in the present paper.

Anti-adhesive agents

Most of oils and many rubbers and also some silicone resins are characterized by a low surface tension and anti-adhesive properties – lack of adhesion to many materials. We described the suggestions to utilize this phenomenon in many prospects and publications. We recommended oils, pastes and oil emulsions for greasing or sprinkling moulds in the rubber and plastics industry. We developed also the special anti-adhesive agents in volatile solvents intended for plastics, rubber [37, 38], and welding industry [39]. They are successfully employed in shipyard sector. The anti-adhesive agents are very economic in use, as e.g. the emulsions for moulds are diluted to 1-2% concentration before sprinkling and they abbreviate the technological processes and decrease the losses. Similarly, the agents in aerosols occurred to be very economic and convenient. Owing to the mentioned advantages, the demand on the described means was growing. For example, after starting up the production of methylsilicone emulsions for tyres-manufacturing sector, the demand on the mentioned products was equal to ca. 200t/year in the nineties.

Methylphenylsilicone varnishes as anti-adhesive means were widely applied in coating of bakery moulds [40] what will be discussed later on in the present paper.

Anti-foaming agents

As early as in the seventies we were asked to develop the replacers of imported silicone antifoaming agents, especially by

the users of papermaking, textile and sugar industries. We elaborated the method of synthesis of branched methylsilicone oils and paste with colloidal silica and water emulsions, having the capability of foam extinguishing. The implementation trials were conducted at the Department of Silicones in the Chemical Works Sarzyna, managed by T. Romańczuk. We participated also in the attempts of application in the paper and textile industry factories. The discussed method was covered with the patent rights in Poland and in the Soviet Union [41, 42].

Products for health protection

Physicians and pharmacists revealed interest in silicones as early as at the beginning of our trials at ITS. We sent the samples of methylsilicone oil for treatment of burns as well as the results of producing the protective ointments. Our methylsilicone oil emulsions were utilized in hydrophobization of the bottles for storage of preserved blood and ampoules for antibiotics. We collected literature information and made interesting contacts with the physicians; in effect, there were developed publications [43, 44] and co-authorship in monograph on the application of plastic materials in medicine [45].

After commencement of production of methylsilicone oils at ZDS, we obtained the consent of the Institute of Hygiene for admission of specially refined methylsilicone oils to application in medicine; they were found in the list of the products, distributed to hospitals and pharmacies. Moreover, one of cream-manufacturing plants in Warsaw undertook production of protective ointment made from our oil.

Biocidal products

In the monographs and publication on silicones, as well as in company prospects since the fifties, the opinion was repeated that silicones, and in particular, polydimethylsiloxane-containing varieties, being widely used in cosmetics and also, in medicine, are not subjected to degradation. When discussing with the organic silicone specialists from the Gdańsk Medical University, we recognized as being purposeful to undertake the studies on resistance of different varieties of polysiloxanes to the effect of certain species of common bacteria. We prepared some samples of cyclic and linear polysiloxanes with different organic substituents nearby silicone and with different molecular weight. In 1993 and 1994, the attempts to examine the effect of 6 species of common heterotrophic bacteria on the mentioned above compounds were conducted in Gdańsk Medical University under the guidance of J. Łukasiak. The analytical control of the possible changes in the composition of the samples was carried out. It was found that the most of the examined polysiloxanes was subjected to a differentiated biodegradation, dependent on their composition, structure and molecular weight and also on the species of bacteria. The results of the mentioned studies were published and submitted during several conferences [46, 47].

Our report presented during the international symposium IUPAC in Stockholm in 1997 on the degradable polymers, as

published in post-symposium materials [48] caused invitation to write a chapter on the biodegradation of polysiloxanes in volume 9 of Encyclopaedia "Biopolymers", to be published by Wiley-VCH Verlag Co. The mentioned task was perfectly implemented by J. Łukasiak [49].

During the described above tests of microbiological degradation of different polysiloxanes, we observed the evident resistance of siloxanes with the 3-chloropropyl substituents nearby Si atom to the activity of various bacteria. In 1995, we undertook the trials to synthesize some chloropropylsiloxanes and sent them to Gdańsk Medical University where the team of J. Łukasiak examined and stated their bacteriostatic effect. We developed the guidelines for synthesis of the mentioned biocides and prepared the patent application [50].

Other biocides, based upon ammonium salts of silsesquioxanes were developed in 2002–2003 by the team of J. Chojnowski at the Centre of Molecular and Macromolecular Studies in Łódź in cooperation with my team and the team of J. Łukasiak from Gdansk Medical University. Two varieties the mentioned salt were developed: one with the utilization of 3-chloropropylsilsesquioxane and n-octyl dimethylamine and the other one, with 3-aminopropylsilsesquioxane and butyl bromide or amyl bromide [51, 52].

Development of the silicon applications

Seventy years ago, apart from developing the technology of synthesis of basic silicone varieties and preparation of their manufacture, our important task included transfer of information about the possibilities of applications and cooperation with the users. The results of our elaborations were submitted immediately after their termination in the patent descriptions and publications. We published the summary up of our achievements, too [53, 54, 55]. In 2002, myself and my co-workers published the second monograph about silicones in which we described also certain Polish applications.

In 2002, the second monograph about silicones was published; we described therein certain Polish applications.

At our Institute, we conducted the informational activity on the applications of silicones and sent the samples from the first syntheses of silicone oils and resins to the interested units. For example, the first applications of the oils obtained in 1954 were the trials of their utilization in treatment of burns and bedsores in the hospital in Warsaw-Prague district and sealing with silicone of bottles for preserved blood and ampoules for antibiotics in the Tarchomińskie Pharmaceutical Works. We were also involved in cooperation, with the interested users, in the field of seeking for the ways of utilizing our silicones. So, after commencement of production of potassium methylsiliconate, the Station of Filters in Warsaw used the mentioned product in hydrophobization of the concrete-made objects and the Air Force Institute of Technology utilized it for protection of runways at the airports from icing. Potassium methylsiliconate was also applied in hydrophobization of the facade of our Parliament building in Warsaw. The mentioned siliconate, as diluted with water to the concentration

of ca. 5%, penetrates the porous surfaces of building materials at the depth of few millimetres and improves the heat stability of the construction and resistance to dirt. The mentioned properties are maintained at least for several years. After the start of methylsilicone resin *Silak M10* production at the Experimental Plant (ZDS) we utilized its solutions in volatile solvents for hydrophobization, especially of porous construction materials, gypsum and for building, as well.

When cooperating with the Factory of Paints and Varnishes (RAFIL) in Radom and Gdańsk, we utilized later improved *Silak M101* in production of heat-resistant and anticorrosive paints with aluminium or zinc fillers, or those with titanium white powder. We also cooperated with Radom Factory in respect of development and production of multicoloured silicone facade paints [57, 58, 59, 60].

Methylphenylsilicone resin *Silak O* (beside *Silak M101*) was mainly applied in production of highly heat resistant (in the range of 350–500°C, depending on the pigment) enamel, also with the resistance to chemicals. The mentioned enamel was destined for steel constructions and chemical apparatuses and, in composition with phthalic paints – in shipyard industry and in heating. *Silak O* was also employed as sealing material for connecting glass and metal elements in electric bulb holders and in mercury lamps. Another methylphenylsilicone resin, *Silak 26*, was used in anti-adhesive coatings, e.g. for varnishing of moulds for plastic castings, especially those made from epoxy resins. Based upon the knowledge obtained from German silicoorganic specialists, we suggested – to Polish experts of food industry – the application of our resins: *Silak 26* and *Silak O* in varnishing of pans, saucepans and similar vessels for frying and baking without fat (Teflon was not produced yet at the discussed time) [40]. It brought considerable profits owing to the possibility of repeated baking in the lacquered moulds. In one of the waffles-producing plant, everyday covering of moulds with fat was eliminated and replaced by their cleaning and varnishing every few months.

Silak 30, similarly as *Silak 26*, was tested in hydrophobic and adhesive coatings and also, as electro-insulating varnish in electrical engineering e.g. in production of bulbs.

The application of silicone pastes in coating of porcelain insulators of a high voltage with the aim to protect from dirt with soot, concrete and other electro-conducting dusts, causing failures and cracking of insulators during rain or fog occurred to be very advantageous. Coating of insulators every few months with a new layer of hydrophobic paste with dielectric properties protected effectively the energetic sub-stations and lines from expensive failures and breaks in the supplies of the electric current. In Poland, the discussed application was implemented at the end of the seventies of the 20th century. The demand on *Sil-pasta E* being produced at the Department of Silicones in Sarzyna Chemical Plant was increased by few tons per year.

We cooperated also for some years with the Wrocław Department of the Institute of Electrotechnic and Plastic Materials Manufacturing Plant (IZO-ERG) in Gliwice. In effect, we were successful in applying *Silak 40* in the Elmor enterprise in Gdansk for electroinsulated impregnation of motor windings for ship lifts

(instead of the formerly used varnish of Dow Corning company), for windings in dry transformers in Mikołowo, and also, in Elkal company in Łódź for heaters of reactors in polyester production. The development of production technology of glass-silicone oilcloths, silicone bands and shirts, with the use of *Silak 50* was the important common achievement. We managed to develop a special catalyst, abbreviating the time of drying of glass textile, coated with *Silak* up to 3 minutes at temperature of 150°C in coating machine for production of oilcloths what enabled to undertake their production. Coating of glass bands and shirts was conducted while immersing their segments of ca. 1 m length in the solution with *Silak 50* with catalyst and then, drying them in a drying machine. The obtained electro-insulating materials were characterized by a good elasticity, good dielectric properties and a perfect thermal resistance. They could withstand up to 1000 hours of heating at 250°C and met the requirements of standard of electro-insulating materials of the highest class H. The discussed materials were widely employed in construction of electric and electronic machines and devices [61]. We tried to utilize more reactive methylphenylsilicone resins: *Silak 15, 20* and *31N* and we developed (in cooperation with the specialists from ERG enterprise in Gliwice) the production technology of glass-silicone plates of 2–10 mm thickness and also, of the pipes rolled up under lower pressure [62].

Building and conservation of monuments belonged to the more important domains where the silicones were applied. We were also involved in this undertaking. Apart from the described above attempts of employing silicones, the solutions of methylsilicone resin in volatile solvents were the successive hydrophobic agents which were developed. They were used in 5-10% concentration for water proofing impregnation of porous materials (such as e.g. cellular concrete or plaster) and for coating of asbestos-concrete plates etc. [63, 64, 65, 66]. They were also successfully applied in waterproofing of radio engineering ceramic elements.

We developed – for the needs of conservation of monuments – the composition, containing solution of *Silak M101* in petrol or inflammable volatile solvent, with the addition of a special, mechanically fortifying agent [67]. Multi-coloured silicon facade paints, produced in the Radom Factory of Paints and Varnishes, as being obtained from our *Silak M101* were in 1974–1976 tested in Warsaw and received a very good evaluation of the performers and inhabitants. They were widely employed in the housing, industrial and monumental building. The mentioned paints were distinguished by non-wettability for water and good vapour permeability (in the contrary to alkyd or acryl paints). They improved thermo-insulating properties of the walls and were characterized by a perfect stability. We could observe, later on, well-preserved, clean walls, as painted 20 years ago as well as the historic relics and monuments. In the eighties, we developed cooperation with the specialists in construction and conservation of monuments [68, 69, 70] by elaborating and implementing the production of the new hydrophobizing-strengthening agents for building materials, especially for limestone, sandstone, bricks and plasters. Additionally, we developed putties and silicone glue for stones

[71] and sent the samples to be tested by the conservators. We consulted the application of the mentioned agents in Powązki cemetery and Wilanowski Palace in Warsaw, at Wawel in Cracow, at the market place in Zamość, in Toruń and in many other sites. We participated also in different exhibitions, conferences and congresses concerning the preservation of national and foreign historical monuments. I had the pleasure to participate twice (with M. Zielecka) in the conservatory work in Egypt, together with the archaeologists from the University of Warsaw and it was the most interesting form of my cooperation with the conservators. The task implemented in the years 1986 and 1987 included the strengthening waterproofing of the walls of the 4 thousand years-old grave mastaba Nefermaat in Meidum near Cairo, which was made from a mud brick, dried at the sun. To this end, our product, *Ahydrosil*, was employed.

In the eighties, we came back to the tests aimed at improving of the recipe for hydrophobic finish of textiles. After their implementation at the Department of Silicones in Sarzyna, we joined a wide application activity in several factories of the textile industry and cooperated with the specialists from some research centres [72, 73, 74, 75]. It was the interesting, few-year lasting activity, staying in the competition with the more abundant offer of experienced western companies. In effect, in spite of quite good hydrophobic effects and meeting the other suitability requirements in certain application trials, we were not able to break the monopoly of the western companies. Only single factories of wool industry as well as mineral wool-producing enterprises employed our agents for waterproofing purposes.

Final remarks

After termination of Poland's isolation in 1990 and opening of the access to the world markets, there was also changed the access of the users to a wide offer of silicones produced not only in the USA and in Europe but also in Japan, China, the South Korea, Brazil and other countries. Those interested in utilization of silicones may take advantage of advises and offers of many companies and specialists and chose in the abundant assortment of the offered silicones. Our role consisting in information and implementation of silicones lost its primary meaning.

At the end of this present publication, I would like to mention that it describes only a certain fragment of the beginnings of development and implementation of production technology and application of silicones in Poland. Apart from my team and the cooperating persons at the Institute of Plastic Materials (since 1970, at Institute of Industrial Chemistry), whose names are found in the enclosed bibliography, the research and implementation work was conducted by the employees of the Experimental Station of Silicones (ZDS) and Department of Silicones at Chemical Works in Nowa Sarzyna, transformed (in 2000) into "Polish Silicones" enterprise. The teams of siliconorganic chemists were developed at the University of Technology in Łódź and Gdańsk, Poznań University, Centre for Molecular and Macromolecular Studies in Łódź and Gdańsk Medical Academy. The scientists from these centers have been conducting their own

studies and also joined the development of production technology of silicones implemented in ZDS Nowa Sarzyna. Apart from the international siliconorganic symposia, being held every three years, there were organized, since 1956 to 2005, the symposia of Polish siliconorganic specialists (also every three years). During the mentioned meetings, the results of the research work and the new projects and tasks were submitted. In the eighties, the enterprise "Unisil" was established at the Nitrogen Industry Works in Tarnów. It was managed by G. Oczkowicz. The mentioned plant produced ethyl silicates from silicontetrachloride and ethanol at a semi-technical scale; they were destined for adhesive of moulds for casting industry. In the successive years, the team guided by B. Marciniak from the University in Poznań implemented the technology of carbofunctional silanes, with production in "Unisil" and utilization of trichlorosilane produced in the Factory in Tarnów. At the same time, "Topsil" company, situated near Warsaw and managed by T. Padee, commenced production of different silicone rubber products from the imported rubbers which is successfully continued until now.

The "Polish Silicones" enterprise, managed by A. Miazga, developed independently production of hydrophobic and silicone facade paints for building and conservation of monuments and of two-component cross-linking rubbers without heating and of rubber sealants (putties), cross-linking as affected by humidity. In the years 2001–2002, the mentioned factory started production of methylvinylsilicone rubbers (on the Chinese licence) in the quantity of ca. 400 t per year and later on, their processing into silicone rubbers. The discussed enterprise is still the main producer of silicones in Poland.

At present, the silicones are well known in our country not only for the plumbers or producers of windows, conservators of monuments and physicians but also users of cosmetics or baby pacifiers. A free market and prices decide on the choice of supplier. Undertaking the studies and a small production almost 70 years ago, the participation of our scientists and Polish siliconorganic specialists in development of technologies and applications and constant informing about the advantages of silicones have, in our opinion, contributed to their wide application and benefits for economy.

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