

Analysis of Development of Russian Fluoropolymer Chemistry, Production and Fields of Fluoropolymers Application: Some Aspects of the History of Creating Russian Fluoropolymers

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Abstract—Information is reported on the history of creating chemistry and processing of fluoropolymers in Russia since 1947 till the present time. The leading role in development of fluoropolymers in Russia belonged to the Research Institute of Polymerisation Plastics (NIIPP), State Institute of Applied Chemistry (GIPKh), and Kirovo-Chepetsk Industrial Complex.

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On April 6, 1938 a Dupont research fellow Roy J. Plunkett working with Freons found a white powder on the walls of the gas cylinder filled with tetrafluoroethylene. Further investigations showed that the powder was poly(tetrafluoroethylene) formed from the tetrafluoroethylene by spontaneous polymerization.

The new polymer attracted attention at once owing to unique complex of properties, namely, it possessed unrivalled chemical stability, excellent antifriction, anti-adhesion, dielectric, and insulation characteristics, hydrophobicity, and it retained these qualities in a wide temperature range, from -260 to $+260^{\circ}\text{C}$.

The first pilot plant of Dupont was installed in USA in 1943, just six years after the discovery of the polymer (the product was manufactured under “Teflon” trade mark). Its industrial in Britain was started by ICI Co under Dupont license to the end of 1947.

The poly(tetrafluoroethylene) got to the USSR in the military articles supplied through Land-lease. Due to the exclusive qualities of this material providing the possibility to solve many problems in manufacture of specialty products a target was set to produce the polymer in the USSR. The USSR addressed the USA in order to buy the license for manufacture of the product, but the answer was negative. Therefore the USSR government charged three organizations with development of the synthesis of the monomer and the

polymer, and with methods of reprocessing of the polymer into goods. The researchers of NII-42 were developing the synthesis of the monomer and the polymerization process under low pressure. The polymerization under high pressure was developed in the institutes of the Academy of Sciences of the USSR. The process of the monomer and the polymer production under medium pressure was carried out in the Research Institute of Polymerisation Plastics (NIIPP) that further became a part of the Public Joint-Stocks Co “Plastpolimer”.

NIIPP won this creative competition and already in the middle of 1948 finished the research part of the synthesis of the monomer and the polymer. In March 1948 appeared the Order of the Council of Ministers of the USSR charging the Ministry of the Chemical Industry with obligation to mount in the State Institute of Applied Chemistry (GIPKh) an installation for the synthesis of tetrafluoroethylene by pyrolysis of Freon 22 with distillation by the NIIPP procedure, and to mount in NIIPP an installation for tetrafluoroethylene polymerization, and also to guarantee the development of processes for processing articles from the powdered polymer.

In March 1949 the pilot installations for the synthesis of monomer and its polymerization were ready, and the development of the process technology was started. These pilot installations were used for production of poly(tetrafluoroethylene) under the trade

mark fluorplast-4 (F-4) up till the putting into the operation in 1956 of the industrial scale plant at the Kirovo-Chepetsk Industrial Complex. Due to the great success in the synthesis of the monomer and the polymer in NII-42 and NIIPP and because of implementation of the process in industry further research in this field in NII-42 was finished.

From 1949 a new R&D field was started in NIIPP, the processing of poly(tetrafluoroethylene) into various articles; the results obtained became the base of a new industrial engineering process. All the work on the development of the polymerization process and the methods of polymer processing were carried out by the small team of the laboratory no. 2 of 12 people under the supervision of Lev Viktorovich Chereshevich who became later the Principal Chemist of the USSR for fluoroplastics problems.

In ninteenfifties the field of studies on fluoropolymers in NIIPP grew, and on May 15, 1961 the laboratory no. 2 was reformed into a Department whose staff in some times contained 140 people. In these years based on six monomers developed in GIPKh in NIIPP were obtained over 60 various fluorine-containing products, including homopolymers F-1, F-2, F-3, F-4 and copolymers F-23, F-32, F-30, F-40, F-4MB.

In 1961 at the Kirovo-Chepetsk Industrial Complex the implementation was started of production of other fluorine-containing polymers and copolymers urgently needed by the industry and the economy of the state. At the same time the work on the synthesis of new polymers and their processing continued at the pilot plant of NIIPP. Due to the growing demand of fluoropolymers in 1963 at the Ural Chemical Plant additional installations were put into operation producing F-4 and F-4D. In the same years at a number of industrial facilities production was started of electrical insulation and capacitor films, pressed articles, composites, fabrics impregnated with fluorinated lacquers, foil-coated dielectrics, sealant materials, electric insulation tubes based on fluoropolymers.

NIIPP (by the Order of the Ministry of the Chemical Industry since August 5, 1969 joined to Okhta R&D Complex "Plastpolymer") became the leading enterprise of the vigorously developing industrial branch: it was obliged to coordinate all the work on the synthesis, processing, and designing of plants for production of fluoropolymer products. On the eve of nineteen eighties at the ONPO "Plast-

polymer" a new field of research appeared, fluoropolymers with functional groups for production of ion-exchange membranes and chemical current sources.

New promising methods were developed for articles production from fluoropolymers: plunger extrusion for polymer F-4 and composite materials, automatic pressing. At the Okhta Chemical Complex was started the production of pipes of diameter up to 600 mm, tubes for high pressure of fluoroplastic 4D, and lined goods. At the pilot plant a wide range of extrusion films from fluoroplastic 4MB were produced, the production was tested of new copolymers F-10, F-100, F-50 for aircraft and cosmic industry. It should be stated that to the beginning of nineteen nineties the fluoropolymers manufactured in the USSR both in the quality and in diversity were no worse than the best world standards, being somewhat less in the production volume than that of USA.

With the commencement of the market relations the fluoropolymer industry bore significant losses: production decreased, the coordination of work was distorted, corporate relations between the enterprises were broken. At the same time due to the export trends in the enterprises a hypertrophy occurred in the production of some grades of fluoroplastic-4, negatively affecting the domestic market and resulting in decreased range of fluoropolymer products. Besides the setback in production, especially in the defense industry that always was pushing forward the fluoropolymer industry, negatively affected the condition of this branch of science.

The characteristic feature of this time is the appearance of a multitude of small firms that as a rule apply old developments with exhausted innovation resource. However among them appear enterprises that based on their proper developments create processes and equipment permitting them successfully compete with the leading world production companies. These are first of all Joint-Stocks Co "Ekspress-Eko" producing filtern materials of fluoropolymers, and NPK "Ekoflon" making unique implants of fluoro-plastic 4D.

Among the industrial successes of the late years the production should be mentioned at the Public Joint-Stocks Co "Plastpolimer" of articles of expanded (elongated) fluoroplastic 4D for a wide range of applications.

In order to recover the lost position in the fluoropolymer industry under the conditions of sharp competition with western companies and China it is

necessary to join the forces of the academic and industrial science for development of industrial processes of chemical and physical modification of fluoropolymers with the use of nanotechnology. To this end in 2007 a number of academic and industrial

institutes involving also representatives of the domestic fluoropolymers manufacturers formed a Consortium "Fluoropolymer Materials and Nanotechnology" whose main goal is the overcoming of the mentioned problems.