

Commercial fluorinated compounds

Dr. Sc., Prof. B.N. Maximov

Russian Scientific Centre "Applied Chemistry"

Fluorine chemistry as a separate branch of chemical industry has been intensively developed from the middle of this century. For this period this branch of chemistry has become one of the most important industries providing modern technological progress in all areas of novel technique such as space, aircraft industry, microelectronics, medicine etc..

At present production of fluorine-containing compounds over the world is enumerated in hundred thousands tons annually with continuous nomenclature expansion. In Russia the production of fluorinated compounds of different classes such as halons, fluoro-olefms and fluoropolymers, fluorinated compounds with functional groups, fluoroaromatic compounds and other is established at several chemical factories, the most important of them are Kirovo-Chepetsky chemical plant, JSC "Halogen"(Perm city), JSC "Chimprom"(Volgograd), JSC "Kaustik" (Volgograd), RSC "Applied Chemistry"(St-Petersbiurg and its branch at Perm-city).

The main volume of the production is chlorofluorocarbons which are used as refrigerants, in production of foam plastics, as fire extinguishing agents etc.. The Montreal Protocol issued in 1987 on substances depleting the ozone layer changed sharply the status of this group of products. According to the Montreal Protocol the production and consumption of chlorofluorocarbons CFC-11,12,113,114,115 and halons 1301,1211, 2402 has been stopped since 1996 in the developed countries, for low developing countries the period of production and consumption phase-out is appointed as the beginning of the next century. By the same time the duration of consumption of "transient" hydrochlorofluorocarbons HCFC -22,142b, 141 b, etc will expire.

After the Montreal Protocol issue, taken into account great demand in nonflammable, nonexplosive, nontoxic refrigerants to substitute ozone depleting substances, active efforts were made in many countries on the development of technologies to produce ozone safety hydrofluorocarbons similar to the prohibited CFCs according to their properties.

As a result of conducted investigations at the RSC "Applied Chemistry" there was developed a number of technologies of ozone safety compounds with a zero ODP such as HFC-23 (CF_3H), 32 (CF_2H_2) 152a ($\text{CF}_2\text{H-CH}_3$), 143a ($\text{CF}_3\text{-CH}_3$), 134a ($\text{CF}_3\text{-CFH}_2$), 125 ($\text{CF}_3\text{-CF}_2\text{H}$), 227ea ($\text{CF}_3\text{CFHCF}_3$), FC-218 (C_3F_8) and also blends on their base providing the necessary exploitation properties for refrigeration, in production of foam plastics, for fire extinguishing and so on.

At present a great attention is paid to the development of blend refrigerants with ODP=0. RSC "Applied Chemistry" has created nonflammable blend refrigerants on the basis of HCF-152a, 134a, 125, 227ea, FC-318c, propane, iso-propane, which are equivalent to R-502, CFC-12 on their exploitation characteristics and compatible with mineral oils, the latter point is of great importance.

The phase out of CFC's production and introducing the technologies for ozone safety compounds production allowed to eliminate a big number of facilities of carbon tetrachloride production which was attributed to ozone depleting substances.

Saturated HCFCs are also raw materials for producing fluoro-olefins which are the basis for production of great amount of various types of fluoro-polymers. Fluoropolymers have not lost their importance up to the present time because they possess unique properties on high chemical and heat resistance and electric insulation properties. These properties allow to use them in high aggressive media, in electrical engineering, aerospace, medicine and so on.

At present the interest to fluoropolymers is increasing ever more because they can meet the requirements of novel area of modern technique: they are able to work both at low temperatures (minus 100°C and lower) preserving their elasticity and at high temperatures (up to 400-450°C) without any change in their properties.

In this connection at present there are carried intensive investigations on optimal technology to produce oxygen-containing compounds (potential monomers):

- hexafluoropropylene oxide,
- perfluoromethylvinyl ethers $R_f\text{OCF}=\text{CF}_2$ ($R_f=-\text{CF}_3$, $-\text{C}_2\text{F}_5$, $-\text{C}_3\text{F}_7$),

hexafluoroacetone and some other providing creation of a new generation of unique polymer materials on their basis.

In recent years fluorinated compounds with functional groups have been of growing interest, particularly fluorinated surfactants. Much effort has been devoted to the development of technology for manufacturing and using the surfactants based on high molecular perfluorinated acids of $R_f\text{COOH}$ structure, where $R_f= \text{C}_6\text{F}_{13}$, C_7F_{15} , C_8F_{17} , $\text{CF}_3\text{O}(\text{CF}(\text{CF}_3)-\text{CF}_2)_n$.

Applying these fluorinated surfactants on the surface of metals and liquids decreases sharply their surface energy due to a barrier film formation on the surface of the material. As a result wide opportunities have arisen to use this effect in technique:

- to extinguish burning petroleum products,
- to reduce friction in machines and mechanisms;
- to give antiadhesion properties (pressmolds and etc.) and so on.

Among fluorinated compounds a great attention is paid to the group of polyfluoroaromatic compounds: hexafluorobenzene, pentafluorobenzene etc.. This interest is caused by a possibility

Taken into account some problems in technological performance of the existing technology for producing polyfluoroaromatic compounds by fluorination of appropriate polychloroaromatic compounds, new technologies of manufacturing these compounds are developed at Perm branch of RSC "Applied Chemistry".

It is necessary to mention a growing application of fluorine-containing compounds in medicine:

Together with well-known inhalation (anesthetic) substances such as methoxyflurane, enflurane, desflurane, a research for optimal compositions of synthetic blood substitute based on inert fluorocarbons: perfluorodecaline, perfluorooctane etc. is carried out.

In recent years in our country successful research has been held and a progress has been achieved on introduction of inert perfluorocarbons such as perfluorodecaline, perfluorooctane, perfluorobromooctane to ophthalmology to heal injured eyes.

A great interest for medicine is in application of fluorine-containing polymers as a material for synthetic blood vessels (vasculums), for manufacturing advanced remedies of different purposes, fluorine-containing antibiotics.

The problems of expansion of manufacturing fluorinated compounds and decreasing production cost are connected largely with the level of their production technology. The industrial methods of production of hydrofluoro-carbons (HFC, FC, HCFC) by liquid phase or gas phase fluorination are perfect enough, as is the process of manufacturing fluoro-olefins: tetrafluoroethylene, vinylidene fluoride etc.. It is proved at a Joint Venture in China where a favorable work on technology of R-22, tetrafluoroethylene, polytetrafluoroethylene is held. But many fluorine-containing compounds such as hexafluoropropylene oxide, perfluoroalkylvinyl ethers need to develop a new engineering philosophy for enlarging production.

Especially, emphasis is given on industrial scale production to elemental fluorine or higher fluorides of the following elements: Co, Sb, Mn etc.. The technologies of SF₆, CF₄, C₃F₈ and perfluorodecaline production using mentioned fluorination agents run favorably on an industrial scale, at the same time this method is used for a number of low scale production of fluorine-containing compounds (IF₅, PF₅, (CF_x)_n etc.) which have independent application or may be used for production of other fluorine-containing compounds.

Taken into account good prospects for the direction of synthesis of fluorine-containing compounds by means of elemental fluorine, RSC "Applied Chemistry" has developed new effective technologies for high exothermic systems with use of elemental fluorine as a fluorinating agent.

When the current setback in production in chemical industry in Russia is overcome the new technologies with expanded nomenclature of commercial fluorine-containing compounds will be in good progress.