

Nitrogen trifluoride (NF₃): Production and purification

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1. Introduction

NF₃ is a toxic gas, inert under normal conditions, odorless in the absence of admixtures. At an elevated temperature it is a strong oxidizer comparable with fluorine.

General constants:

Boiling point, °C -129 (1), -129.1 (2)
Melting point, °C -206.8 (1), -208.5 (2)
Liquid density, g/cm³ - 1.533 (1)
Evaporation heat, cal/mol - 2769 (1)
Melting heat, cal/mol - 95.1 (1)

Due to easy handling at room temperature, NF₃ has advantages compared with fluorine and is used as a stable fluorinating agent and has a wide application in high-energy chemical lasers, at dry etching in production of semiconductors, as a filling gas in lamps to prolong their durability and increase brightness, as a detergent gas in CVD apparatuses (chemical gas-phase precipitation) (3,4,77).

2. Methods of NF₃ production

For the first time, NF₃ was produced by O. Ruff et al. in 1928 by electrolysis of melt anhydrous NH₄⁺ HF at 125°C, voltage of 7-9 V, current of 10 A in a copper electrolytic cell on a carbon anode (5).

This method was assumed as a basis for modern technologies to produce NF₃, the second industrial method is direct fluorination of ammonia.

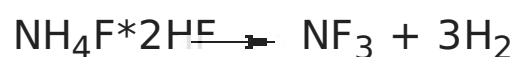
Paper (6) presents a review based on publications right up to 1984 including data on methods of NF₃ production, purification, reactions with elements, organic and inorganic compounds and also its molecular properties, spectra, thermodynamic constants etc. That is why the present review considers only publications from 1983 y.

2.1. Electrolytic methods to produce NF₃

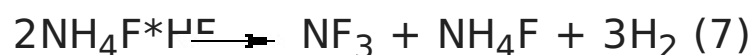
General data (6)

Electrolysis of NH₄F*(1,1-1,8)HF melt is a main method to produce NF₃ on an industrial scale. Carbon materials and nickel are used as anode materials each of them has own merits and demerits. Carbon materials contrary to nickel are not liable to anodic dissolution, but during their use there are observed anode polarization (anodic effect), anodic corrosion

and contamination of the goal product with carbon tetrafluoride. The process is described by the following equation:



or



When carbon-containing materials of the anode are used, N_2 , N_2F_2 , N_2F_4 , NHF_2 , nitrogen oxides, oxygen and CF_4 are formed together with NF_3 and H_2 .

The optimal process parameters are as follows:

Temperature 100-120°C

Current density 0.12-0.15 A/cm²

NF_3 current efficiency ~70%.

The electrolysis process is dangerously explosive due to the formation of a mixture of NF_3 with hydrogen and other components of electrolysis gas in the cell. To decrease the danger, the anodic and cathode spaces are separated with a diaphragm or the NF_3 concentration is kept beyond the bounds of explosiveness by nitrogen introduction into the cell.

Improvement of the electrolysis process

Within the period under review, a number of problems can be chosen which attracted intensive efforts of Japanese companies, particularly of Mitsui Chem. Inc.

1. Problems concerned with increasing safety of the electrolysis process owing to prevention of mixing anode and cathode gases.

This problem can be solved by the following measures:

a) electrolytic cell modernization including

- separation of an anodic and cathode cells with fluoropolymer diaphragm (8)
- cell coating with a polymer resistant at temperatures above 140°C in places of contact with the melt and synthesis gases (9)
- certain location of the cell elements (electrodes, the diaphragm, the head):

-the electrodes are placed below the diaphragm base (10) the electrodes are placed at a distance of 30-200 mm from the separating diaphragm (11)

-the electrodes, head and electrolyte surface are installed at a certain distance from each other (12,13)

-two-level arrangement of the electrode cells preventing mixing anodic and cathode gases (14)

b) a number of engineering approaches after the ending of NF_3 formation:

- continuous or periodical arrangement of a potential between the anode and cathode (16)
 - pressure control at gas-carrier supply into the anodic and cathode cells (15)
 - purge with inert gas of the anodic cell equipped with a special nipple joints for gas output and input after the electrolysis stop till its activation (17)
- Problems concerned with the formation of carbon tetrafluoride difficult to isolate from NF_3 and with the anodic effect in case of the use of carbon-containing materials for the anode. The following ways are used to solve these problems:
 - keeping of the water concentration in the electrolyte within 0.01-1%, that is attained by water removal or addition of the starting material in amount of 0.1-10wt.% continuously or periodically (18). It is possible to decrease the water amount and prevent the anodic effect and also formation of CF_4 when the starting electrolyte is produced from dry gaseous NH_3 and HF (19):
 - to carry out the process at a current density above $50\text{mA}/\text{cm}^2$ (20)
 - to use a high-strength anode:
 - with the resistance to bending of over $1000\text{kg}/\text{cm}^2$ (21);
 - with the resistance to bending of over 50 MPa, current density of $4\text{-}30\text{ mA}/\text{dm}^2$ and the ratio of $\text{HF}/\text{NF}_4\text{F}$ in the electrolyte of 1-3 (22). The anode is made of porous carbon;
 - with the resistance to bending of over 50 MPa, current density of $50\text{ mA}/\text{cm}^2$ max, potential between the cathode and neighboring anode of 6V max, quantity of electricity per 1 cm^2 of the anode surface of over 500 coulomb (23);
 - with the resistance to bending of over 50MPa, porous anode containing fluorides of Li, Na, Al, Mg, Ca, Ni. The process is carried out at a current density of $4\text{-}30\text{ mA}/\text{dm}^2$ and a ratio of $\text{HF}/\text{NH}_4\text{F}$ equal to 1-3 (24).
 - to carry out the process under control of pressure on the anode in dependence of which a necessary current density is provided. (25).
- When metal anodes are used, their dissolution takes place with the formation of metal salts resulting in passivation of the anode and NF_3 yield decrease.

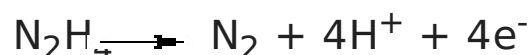
To increase the NF_3 yield it was proposed:

- to remove salts formed on the anode (26)
 - to carry out forced convection of the electrolyte suppressing the formation of the salts (27)
 - to use anodes made of special electrode composition produced by sintering Ni-containing oxides with coating of disperse nickel or nickel powder. The temperature of the process is $100\text{-}140^\circ\text{C}$, the ratio of $\text{NH}_4\text{F}/\text{HF}$ in the electrolyte is 1-3 (28).
- Increase in NF_3 purity produced during the electrolysis process.
 - To increase the purity of NF_3 , it is necessary to use the starting material of high purity produced from gaseous NF_3 of over 99.5 wt. % purity and HF of over 99.8 wt.% purity, nickel electrodes should have purity of 98.5 % min (29,30) or 99.5% min (31).
 - The starting NH_4F contains 50 ppm of carbon maximum (32)

2.2. Investigation of possibility to produce NF₃ using binary systems of electrolyte.

German researchers made attempts to produce NF₃ in a higher yields using compounds with a higher valence as an additional nitrogen-containing component, for example hydrazine difluoride in NH₄F*HF melt (33).

This attempt was not crowned with success since the following reactions take place on the anode in case of hydrazine use:



Another direction of the investigation was possibility to use additives to NH₄F*HF system with the purpose of simultaneous production of NF₃ in a higher yield and a different process product. Sulfamoyl fluoride H₂NSO₂F was taken as the additive (34,35).

H₂NSO₂F*NH₄F*HF system behaved as a binary electrolyte and they failed to increase the current yield. Simultaneously it was possible to obtain NF₃ from NH₄⁺ and SO₂F₂ from H₂NSO₂F, at the same time increase in the H₂NSO₂F quantity resulted in an increase in SO₂F₂ yield but not NF₃.

Similar behavior of NH₄F*HF systems with additives of NH₄N(SO₂F)₂ and (NH₂)₂SO₂ was observed (36).

2.3. Doshisha University (Kyoto) investigations.

In the middle 80-s experts of Doshisha University continued a work started in the 60-s by N.Watanabe et al. devoted to the reactions taking place during electrolysis of salt melts with use of carbon-containing anodes and platinum reference electrodes. The purpose of the work was to determine the optimal conditions of NF₃ formation.

Further study of electrolysis of KH₂F₂-RNH₂ systems, where CH₃CONH₂ and HCONH₂ were used as RNH₂, on an amorphous carbon electrode at 120°C has shown that the anodic effect was observed at a current density of 3-20 mA/cm² and a film of carbon polyfluoride (C_xF)_n was formed on the anode. 1% LiF addition prevented the anodic effect but reduced the yield of NF₃ and the water content in the melt. The maximum NF₃ yield of 50.9% was obtained at a current density of 5.3 mA/cm² and 4 mol% of HCONH₂ additive (37,38). The same yield under similar conditions was obtained when a glossy anode was used (39).

An addition of urea to a system of KH₂F₃ was studied earlier (40).

An addition of urea to a different system of NH₄F-HF-KF gives the same results, i.e. an increase in the NF₃ current efficiency due to removal of water which is consumed for urea hydrolysis and COF₂ forming in the process. The maximum content of NF₃ in the anode gas is 87% (41).

Later on investigations were carried out using NH₄F*2HF melt and a nickel anode.

A possibility to improve the process parameters due to introduction of such additives as

NH_4NiF_3 , $(\text{NH}_4)_3\text{FeF}_6$ and AlF_3 to the electrolyte has been tested.

If the maximum NF_3 yield attained 66% without additives at the anodic dissolution of 3%, then an addition of 0.1mol% of the most effective complex of NH_4NiF_3 reduced the anodic dissolution to 1%, but the NF_3 yield reduced to 60% also (42,43,44). The process with the use of NH_4NiF_3 has been patented (45).

CsF (46,47) and LiF (48,49) were used as additives. The additives of these salts reduce the anodic dissolution and increase the NF_3 yield. The processes using CsF and LiF have been patented (47,49).

Further studies on the effect of fluorides such as KF , MgF_2 , NaF , AlF_3 , CsF and LiF confirmed the effectiveness of CsF and LiF additives and showed that KF reduced the NF_3 yield and stimulated the anodic dissolution (50,51).

A search for metal workable in $\text{NH}_4\text{F} \cdot \text{HF} \cdot \text{CsF}$ melt has found that Al , Fe , Mo , Nb , Sn , Ta and Ti are subjected to vigorous dissolution. Ag , Co , Cu , and Zn are also unusable because of passivation preventing from current passage.

Nickel was found the most acceptable metal for the anode, and also Monel, one of its alloys (52). Electrodes made of Ni-NiO_{1-x} composite produced by HIP (hot isotactic pressing) method were also studied. The anode made of 10% composite was covered with a thick layer of oxides with infrequent porosity that prevented the anode from dissolution and increased the NF_3 yield. An anode made of 20% composite has these parameters much worse. The anodes operated in $\text{NH}_4\text{F} \cdot 2\text{HF}$ melt (53).

An anode made of a different material, carbon impregnated with lithium fluoride, was studied in systems of $\text{NH}_4\text{F-HF}$, $\text{KF-NH}_4\text{F-HF}$, $\text{CsF-NH}_4\text{F-HF}$. The yield of NF_3 on these anodes is lower than that on nickel ones (53).

Further study of the anodic reactions on the nickel anode in melt of $\text{CsF-NH}_4\text{F} \cdot \text{HF}$ at 50-80°C allowed to conclude that an increasing the potential resulted in change of the anodic reactions and four zones were separated in dependence on the voltage:

0-1V (compared with H_2 standard electrode): nickel anodic dissolution

1-3V : deposition of Ni(II) compounds containing oxides (passivation)

3-5V : Ni(II) oxidation to Ni(III) and/or Ni(IV)

over 5V: proper NF_3 fluorination

The anode gas is composed of NF_3 and N_2 with a small additive of O_2 , N_2O , N_2F_2 , N_2F_4 (55). A similar picture is observed in melts of $(\text{CH}_3)_4\text{NF}_m \cdot \text{HF}$ and $(\text{CH}_3)_4\text{NF}_m \cdot \text{HF} + 50\% \text{CsF} \cdot 2\text{HF}$, where $m=3, 5+0.5n$ ($n=1-4$).

Here also 4 zones are seen. An oxidized layer is formed at a potential above 4V and is composed of NiF_2 , fluorides with high oxidation level and a small quantity of oxides of different valence (56). Paper (57) describes a mechanism of fluoride films formation on the anode. This phenomena and possible effect of fluoride layers on the fluorination process have been reviewed in paper (54).

3. Ammonia direct fluorination

Ammonia fluorination in $\text{NH}_4\text{F}\cdot\text{HF}$ melt is far more practically feasible process than gas-phase fluorination. That allowed Air Products and Chem. to implement this process on an industrial scale and produce the product of 99.5% purity (6).

Later on research in this field was directed to

1. expansion of a source of raw materials

- $(\text{NH}_4)_3\text{AlF}_6$, $(\text{NH}_4)_2\text{SiF}_6$ and $(\text{NH}_4)_2\text{NaAlF}_6$ were proposed as a starting solid complex. Their interaction with fluorine is conducted at a temperature below 150°C . The product obtained has a purity of 98.5% (58)
- metal fluorides in a mixture with ammonium salt at fluorination with elemental fluorine diluted with nitrogen give NF_3 in 96.9% yield (59)
- search of solutions on prevention of clogging apparatus
 - to produce NF_3 by gas phase method at a ratio of F_2/NH_3 equal to 3-20, it is envisaged to place a reactor in a heating area at $80\text{-}250^\circ\text{C}$ (60)
 - two plates are placed in the reactor with a gap of 0.1-10cm (61)
 - fluorine and ammonia used in the gas phase process are charged through a spiral along the inside reactor wall for mixing and interaction. The formation of NH_4F_2 resulting in clogging is prevented (62).

A processing line with circulation of a melt containing ammonia, metal fluoride and HF has been patented. The processing line includes the following equipment through which the melt circulates: an electrolyzer to produce fluorine and hydrogen, a reactor for NF_3 production and 2 apparatuses- solubilizers located between them, one apparatus at the output of the melt from the electrolyzer and the second one at the input. Gas-carrier together with ammonia and fluorine respectively are charged into these apparatuses to keep the ammonia and HF concentration constant in the melt. Fluorine mixed with the gas-carrier comes to the reactor where it reacts with the melt to form NF_3 (63).

Paper (64) suggests to carry out interaction of elemental fluorine with ammonia complex $\text{NH}_4\text{F}\cdot\text{HF}$, $(\text{NH}_4)_{1-4}\text{MF}_{2-8}\cdot n\text{HF}$ (where M is an element of I A-V A group, I B-VII B group and VIII group) at mixing of the melt complex with a turbine-type mixer.

4. NF_3 purification methods

Modern electronic industry makes high demands for NF_3 purity right up to 99.999% in which connection a great attention is paid to NF_3 purification.

Methods for NF_3 treatment for removal of acid and hydrolyzable admixtures and difluorodiazine, N_2F_2 , have been described in (6). N_2F_2 was removed by decomposition over a nickel-containing catalyst at 240°C , for example in a nickel pipe filled with nickel balls or other nickel packing. In this case the content of N_2F_2 is reduced from over 0.1% to less than 0.01%.

NF_3 catalytic purification from N_2F_2 with nickel-containing compounds was further developed in the work of Mitsui Toatsu Chem. Inc. . They used heating NF_3 raw at $150\text{-}600^\circ\text{C}$ in a vessel covered with nickel fluorides. The vessel coating was made by its treatment with fluorine (66, 67, 68, 69, 70, 71). To increase the purification level, the vessel may be filled with fluorides (69-72), for example with fluorides of nickel or calcium (74).

To purify NF_3 from N_2F_2 and/or OF_2 it is suggested to use other fluorides:

- tablets made from NaF melt and polyvinyl alcohol preheated at 850°C before use (75)
- silicon fluorides after heating at a temperature over 600°C (65)

Sorbents are widely used for NF_3 purification. A process with their use is carried out in adsorption or chromatographic regime.

- when NF_3 containing 1.7% of N_2F_2 is contacted silica gel, the content of N_2F_2 is reduced to 20ppm (76)
- silica gel preheated and preliminarily dried at a temperature of $150\text{-}300^\circ\text{C}$ effectively removes N_2O and CO_2 at a temperature of 125°C (68,70,77)
- anhydrous aluminum oxide (Al_2O_3) at $250\text{-}900^\circ\text{C}$ and the same adsorption temperature removes N_2O and CO_2 (69,71,79)
- activated carbon after preliminary removal of acid admixtures from NF_3 purifies it completely from N_2F_2 and N_2F_4 (78,83)
- SiO_2 with interstices of 3-10 mm is applied for removal of nitrogen oxides without NF_3 losses (80)

Purification with use of natural and synthetic zeolites (81) is also wide spread.

Before use, zeolites are preheated in a nitrogen flow at a temperature of $270\text{-}700^\circ\text{C}$ (81,85,86). For their reuse, the heating is conducted step-by-step, first at $50\text{-}200^\circ\text{C}$, then at $250\text{-}700^\circ\text{C}$ (87,88). To ensure the uniform heating of zeolites, metal perfluorinated disc-shaped plates are inserted in the zeolites (89). A purification temperature with use of zeolites is $125\text{-}110^\circ\text{C}$.

The following admixtures are removed by means of zeolites:

- N_2O and N_2F_2 , in this case it is recommended to carry out additional treatment of zeolites with solutions of sodium salts of organic and inorganic acids with subsequent heating at $250\text{-}700^\circ\text{C}$ (82)
- N_2O and CO_2 (90,91,92,93,86)
- water for which removal natural (93) and synthetic (94) zeolites of 3A type are used

To separate NF_3 and CF_4 a chromatography method is applied using zeolites of 3A type either containing 1-10% of water (84) or preliminarily wetted with water and heated for 16 hours at 300°C in inert medium of chabazite or zeolite of 5A type with the pore surface of 4.4-4.8 Å. The charge of the flow to be separated is executed in a pulse regime. Purification of the separated gases reaches 99.99% (95).

SiO_2 adsorbents, carbon molecular sieves, Al_2O_3 , macro-cross-linked polymers, kieselgur, active carbon, aluminosilicates and zeolites containing also chemisorbents for decomposition of admixtures may be used for sorption storage of gases in a special adsorption-desorption apparatus. A gas to be desorbed is charged directly to a CVD apparatus or a laser plant (107-109).

Low-temperature rectification in the presence of a third component (He, Ar, Ne etc.) is used for purification of NF_3 from N_2F_2 , CO_2 , O_2 , N_2 (96-98). A complex of procedures for NF_3 purification including sorption purification and rectification in columns of middle and low pressure has been patented (99).

A method to purify NF_3 from CF_4 by azeotropic and extractive low-temperature rectification to the content of admixtures of 10 ppm was described in (111).

The following methods of NF_3 purification were also described:

- to purify from HF and OF_2 , the raw gas is first washed with water or a solution of NaOH , then it is treated in a scrubber with aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$, HI or Na_2S (100)
- application of a reactive *micromatrix* containing *organo-metalic* compounds allows to reduce admixtures to ppb level and even lower (101)
- to remove water from a number of gases including NF_3 , a process including distillation of water and its separation from the gases was patented (102)
- to remove N_2F_2 , purification by UV radiation treatment with subsequent contacting the gas with adsorbents was suggested (103)
- processes of NF_3 separation from a gas-diluent by means of selective membranes are described in (104,105)

Usually the purified NF_3 is stored in cryogenic tanks (91,92) including tanks joined to a heat exchanger for NF_3 condensation (106).

Gases containing NF_3 and admixtures are fractionated by gas chromatography method and analyzed by IR-spectroscopy (46), gas chromatography identification of NF_3 traces is also known (110)

The water content in NF_3 less 50 ppm may be determined by laser spectroscopy (112).

References

1. Kirk-Othmer, Encyclopedia of Chemical Technology, 1980, v.10. p. 768
2. Kratkaia khimicheskaya encyclopedia, 1966, v.5, p. 579, Izd. "Sovetskaya encyclopedia"
3. Ullmann's Encyclopedia of Industrial Chemistry, 1988. v. A II. p. 339
4. J. Fluor. Chem., 1985, v. 27, n. 1, p. 23-33
5. O. Ruff, I. Fisher. F. Luft, Z.anorg. Chem., 1928, v.172, 417-425
6. Gmelin Handbook, 1986, v.4, p. 171-231
7. A.Zemljic, B.Druzina, A.Smallm, Kern. Ind., 1986, v 35. N 5, p. 277-279; CA. 1986, v.105. 87396
8. T.Iwanaga, H.Momotake, A.Tasaka, JP. Appl. 88-130790, 1986/88, Mitsui Toatsu Chem Inc, CA,1989,v.110,15084
9. A. Mitsumoto. A.Aritsuka ,I.Harada, JP. Appl. 94-88267, 1992/94, Mitsui Toatsu Chem. Inc., CA, 1994. v.121,68148
10. T.Iwanaga, I.Harada, T. Yamaguchi. JP. Appl. 90-61082. 1988/90, Mitsui Toatsu Chem.Inc.,CA,1990,v.113. 200125
11. N.Iwanaga, T.Yamaguti, N. Fujieda and others, EP 424727, 1989/91, Mitsui Toatsu Chem. Inc., CA, 1991. v. 115, 122501
12. N. Iwanaga, T. Yamaguti, N. Fujieda and others, US Patent 5054156. 1989/92, Mitsui Toatsu Chem.Inc.. CA, 1992,v.116, 223788
13. T. Iwanaga. T. Kuroda, JP. Appl. 92-160176. 1990/92, Mitsui Toatsu Chem.Inc.,CA. 1993. v.118. 156854
14. G. Tarancon, US Patent 5779866, 1996/98, Florida Scientific Lab. Inc., CA, 1998, v. 129, 128237
15. I. Harada. T. Iwanaga, JP. Appl. 90 232386, 1989/90, Mitsui Toatsu Chem. Inc., CA, 1991, v. 115, 17581

16. M. Aritsuka. T. Iwanaga, JP. Appl. 92 32592, 1990/92, Mitsui Toatsu Chem.Inc., CA, 1992, v. 116, 223786
17. M. Aritsuka, T. T. Nishitsuji, T. Iwanaga, JP Appl. 92 09488, 1990/92, CA, 1992, v. 116, 183525
18. M.Aritsuka. T.Iwanaga, H.Hotconohara, JP.Appl. 90-263988, 1988/90, CA. 1991, v.115,37512
19. M. Zaike, T.Iwanaga, JP. Appl. 92-56789, 1990/92, Mitsui Toatsu Chem. Inc., CA, 1992, v.117, 200536
20. M.Aritsuka, A.Mitsumoto, JP. Appl. 93-51778, 1991/93, Mitsui Toatsu Chem. Inc., CA, 1993, v. 119, 58356
21. M.Aritsuka. T.Iwanaga, A.Mitsumoto, JP. Appl. 92-131391, 1992/90, Mitsui Toatsu Chem.Inc., CA,1994,v.120, 64636
22. M.Watanabe, Y.Tei, M.Kanamaru, M.Aritsuka, A. Mitsumoto, JP. Appl. 93-70982. 1991/93, Mitsui Toatsu Chem.Inc.,CA, 1993,V.119, 104967
23. M. Aritsuka, A.Mitsumoto. JP. Appl. 93-51779, 1991/93, Mitsui Toatsu Chem.Inc., CA, 1993, v.119, 58362
24. N. Watanabe, Y.Tei, M. Kanamaru, M. Aritsuka, A.Mitsumoto, JP. Appl. 93-86490, 1991/93, Mitsui Toatsu Chem.Inc., CA,1993. v.119, 236543
25. M.Aritsuka. A.Mitsumoto, JP. Appl. 93-51782, 1991/93, Mitsui Toatsu Chem.Inc.,CA, 1993, v.119, 58363
26. I.Orihara, S.Sato, M.Saito, N.Ono, JP.Appl. 91-236486, 1990/91, Kanto Denka Kogyo Co. Ltd., CA,1992, v.116, 8505
27. T. Yoshino, H. Kamata, T. Shinozaki, JP.Appl. 96-176872, 1994/96, Mitsui Toatsu Chem.Inc., CA, 1996, v.124,179865
28. A.Tasaka, M.Aritsuka, T.Iwanaga, A.Mitsumoto, JP.Appl. 96-225976, 1995/96, Mitsui Toatsu Chem.Inc., CA, 1996, v.125, 280153
29. T.Shinozaki, Y.Hirata, JP.Appl. 96-134675, 1994/96, Mitsui Toatsu Chem.Inc.,CA, 1996, v.125,126099
30. T.Shinozaki, Y.Hirata, JP.Appl. 96-120474,1994/96, Mitsui Toatsu Chem. Inc., CA,1996, v.125, 62494
31. T.Shinozaki, T.Yoshino, JP. Appl. 97-86909, 1995/97, Mitsui Toatsu Chem. Inc., CA., 1997, v.127, 20515
32. H.Hokohara, T.Iwanaga, I.Harada, T.Yamaguchi and others, JP.Appl. 89-191792, 1988/89, Mitsui Toatsu Chem.Inc., CA,1 990, v.112, 13434
33. P.Sartori, DE off. 3722163, 1987/89, Kali-Chemie AG, CA, 1989,v.110,162522
34. P.Sartori, K.D.Lattasch, J. Fluor. Chem.,1992,v.57(1-3), p. 113-119
35. P.Sartori, C.Juenger, K.D.Lattasch, DECHEMA Monogr.,1992, 125. (Electrochem. Stoffgewinnung Grundlagen Verfahrenstech.) 233-242, CA. 1992. v. 117.159540
36. P.Sartori, K.D.Lattasch, J.Fluor.Chem..1995.V.74, n.1.p.137-139, CA, 1995, v.123, 269235
37. A.Tasaka, H.Sakaguchi, R. Aki, H.Ihara and others, J.Fluor.Chem.,1985, v.27, n.1, p.23-33
38. A.Tasaka. H.Sakaguchi, T.Yamamoto, Proc. Int. Symp. Molten Salt Chem. Technol., 1st, 1983,305-308, CA.1985,v.102,139700
39. A.Tasaka, H.Sakaguchi, H.Ito, N, Norimuna, Nippon Kagaku Kaishi, 1988, n.6, 873-880, CA.1988,v.109,199844
40. A.Tasaka, H.Watanabe, Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 1981, 49, n.8, 511-516, CA,1981,v.95,158699
41. A.Tasaka, H.Ito, H.Kobayashi, Nippon Kagaku Kaishi, 1985, n.10, 1785-1804, CA, 1985, v.103, 223152
42. A.Tasaka, H.Kabayashi, M.Hori and others, Proc-Electrochem Soc..1987, 87-7 (Proc. J. Int. Symp. Molten salts), 949-958,CA, 1987,v.107,163987
43. A.Tasaka, M.Negami, K.Nagasaki and others, Proc.Electrochem Soc.,1994, 94013. (Molten Salts), 601-608, CA, 1995,v.122,40888

44. A.Tasaka, H.Kobayashi, M.Negami and others, J. Electrochem Soc.,1997, v.144, n.1,192-197,CA,1997, v.126, 244038
45. A.Tasaka, H.Nakayama, JP.Appl. 88-274789, 1987/88, Showa Denco K.K., CA, 1989.v.110,143550
46. A.Tasaka, K.Mizuno, A.Kamata, K.Miki, J.Fluor.Chem.,1992, v.57 (1-3), 121-130
47. A.Tasaka, T.Tateno, JP.Appl. 91-104891, 1989/91, Morita Kagaku Kogyo Co. Ltd., CA,1991,v.115,169018
48. A.Tasaka, T.Osada and others, Proc.-Electrochem. Soc.,1996, 96-7 (Molten Salts), 144-151,CA,1996, v.125, 259549
49. A.Tasaka, M. Aritsuka, T. Iwanaga, A. Mitsumoto, JP. Appl. 96-225973, 1995/96,CA, 1996, v. 125, 280152
50. A. Tasaka, M. Yamanaka, T. Osada, Proc.-Electrochem. Soc. , 1997, 97-15 (Electrochemistry in the preparation of Fluorine and its compound), 144-157, CA, 1997, v. 127, 254450
51. A. Tasaka, T. Osada, M. Kobayashi and others, J. Fluor. Chem.,1998, v.87, n.2, p.163-171
52. A. Tasaka, K. Mizuno, A. Kamata, Mater. Sci. Forum, 1991, 73-75 (Molten Salt Chem. Technol.), 603-608
53. A. Tasaka, H. Oshida, Y. Suzuki and others, Proc.-Electrochem. Soc.,1998, 97-28, 109-118, CA, 1998, v.128, 276312
54. A. Tasaka, T. Kawagoe, A. Takuwa, M. Aritsuka, J. Electrochem. Soc., 1998, v. 145, n. 4, p. 1160-64, CA, 1998, v.129, 20828
55. A. Akimasa, K.Mizuno,A. Kamata and others, Proc.-Electrochem. Soc., 1992, 16 (Proc. Int. Symp. Molten Salts, 8th,1992),564-73
56. A. Tasaka,T.Yachi, T. Makino and others, Proc.-Electrochem. Soc.,1998, 98-11 (Molten Salts XI), 658-666, CA, 1999, v.130, 58381
57. A.Tasaka, Y. Tsukuda,S. Yamada and others, Electrochem. Acta, 1999, v.44, n. 11,1761-1769, CA, 1999, v.130, 202125
58. M. Aramaki, Y. Kobayashi, T. Nakamura, DE off. 3435298, 1983/85,Central Glass Co. Ltd., CA, 1985, v.102, 206098
59. I. Orihara, S. Sato and others, JP.Appl. 91-232710, 1990/91, Kanto Denka Kogyo Co. Ltd., CA, 1992, v.116, 109560
60. M. Shimizu, JP. Appl., 90-255512, 1989/90, Asahi Glass Co. Ltd., CA, 1991, v.114, 84845
61. M. Shimizu, JP. Appl., 90-255511, 1989/90, Asahi Glass Co. Ltd., CA, 1991, v.114, 84846
62. K. Katsumi, K. Okana, T. Mukono, T. Kurada, JP. Appl. 93-105411, 1991/93, Onoda Cement Co. Ltd., CA, 1993, v.119, 99212
63. G. Tarancon, US 5628894,1995/97, Florida Scientific Lab., CA, 1997, v.127, 25046
64. D. G. Coronell, T.H.L. Asiung, H.P.Withess, US 5637285, 1996/97, Air Prod. And Chem. Inc., CA, 1997, v.127, 83493
65. T. Nishitsuji, M. Aritsuka, JP. Appl. 92-198006, 1990/92,Mitsui Toatsu Chem Inc., CA, 1992,v.117, 236701
66. I. Harada, H. Hokonohara, T. Yamaguti, EP Appl. 337294, 1988/89, Mitsui Toatsu Chem. Inc., CA, 1989, v.111, 236120
67. I. Harada, H. Hokonohara, T. Yamaguti, JP. Appl. 89- 261206, 1988/89, Mitsui Toatsu Chem. Inc., CA, 1990, v.112, 237761
68. T. Nishitsuji, T. Iwanaga, I. Harada, JP. Appl. 90 164707, 1988/90, Mitsui Toatsu Chem. Inc., CA, 1990, v.113, 214867
69. T. Nishitsuji, T. Iwanaga, N. Koto, JP. Appl. 90-22111, 1988/90, Mitsui Toatsu Chem. Inc., CA, 1990, v.113, 81617
70. T. Nishitsuji, T. Iwanaga, I. Harada, JP. Appl. 90 164708, 1988/90, , Mitsui Toatsu Chem. Inc., CA, 1990, v.113, 214868
71. T. Nishitsuji, T. Iwanaga, I. Harada, JP. Appl. 90 18309, 1988/90, Mitsui Toatsu Chem.

- Inc., CA, 1990, v.113, 135114
72. T. Suenaga, JP. Appl. 90-116216, 1997/99, Central Glass Co. Ltd.
 73. I. Harada, H. Hokonohara, T. Yamaguchi, JP. Appl. 89 261208,, 1988/89, Mitsui Toatsu Chem. Inc., CA, 1990, v.112, 237762
 74. I. Harada, H. Hokonohara, T. Yamaguchi, JP. Appl. 92 275909, 1991/92, Mitsui Toatsu Chem. Inc., CA, 1993, v.118, 41816
 75. T. Nishitsuji, M. Aritsuka, JP. Appl. 92 12010, 1990/92, Mitsui Toatsu Chem. Inc., CA, 1992, v.116, 154912
 76. I. Harada, T. Iwanaga, H. Homotake, JP. Appl. 88 151608, 1986/88, Mitsui Toatsu Chem. Inc., CA, 1988, v.109, 131692
 77. T. Nishitsuji, T. Iwanaga, I. Harada, JP. Appl. 90 153809, 1988/90, Mitsui Toatsu Chem. Inc., CA, 1990, v.113, 155343
 78. F. Morikawa, E. Hirai, JP. Appl. 95 330316, 1994/95, Nissan Chem. Ind. Ltd., CA, 1996, v.124, 236439
 79. T. Nishitsuji, T. Iwanaga, N. Koto, JP. Appl. 89 261209, 1988/89, Mitsui Toatsu Chem. Inc., CA, 1990, v.112, 237763
 80. T. Nishitsuji, T. Iwanaga, M. Aritsuka, JP. Appl. 91 275507, 1990/91, Mitsui Toatsu Chem. Inc., CA, 1992, v.116, 154922
 81. T. Shinozaki, H. Kamada, JP. Appl. 96 91812, 1994/96, Mitsui Toatsu Chem. Inc., CA, 1996, v.125, 37429
 82. T. Nishitsuji, T. Iwanaga, M. Aritsuka, JP. Appl. 92 175211, 1990/92, Mitsui Toatsu Chem. Inc., CA, 1992, v.117, 174553
 83. K. Kamatura, K. Sugano, H. Nakayama, JP. Appl. 86 247609, 1986/86, Showa Denco K.K., CA, 1987, v.106, 122463
 84. T. Suenaga, T. Fujii, Y. Yobayashi, JP. Appl. 91 208806, 1990/91, Central Glass Co., CA, 1991, v.115, 259374
 85. M. Aritsuka, N. Iwanaga, EP 366078, 1988/90, Mitsui Toatsu Chem. Inc., CA, 1990, v.113, 43437
 86. M. Aritsuka, N. Iwanaga, JP. Appl. 92 144905, 1990/92, Mitsui Toatsu Chem. Inc., CA, 1992, v.117, 114704
 87. N. Fujieda, T. Yamaguchi, JP. Appl. 92 187510, 1990/92, Mitsui Toatsu Chem. Inc., CA, 1992, v.117, 194705
 88. N. Fujieda, T. Yamaguchi, M. Aritsuka, JP. Appl. 92 254404, 1991/92, Mitsui Toatsu Chem. Inc., CA, 1993, v.118, 8944
 89. I. Harada, JP. Appl. 92 228408, 1990/92, Mitsui Toatsu Chem. Inc., CA, 1992, v.117, 254315
 90. I. Harada, T. Nishitsuji, T. Iwanaga, N. Koto, JP. Appl. 90 30609, 1988/90, Mitsui Toatsu Chem. Inc., CA, 1990, v.113, 135203
 91. M. Aritsuka, T. Iwanaga, JP. Appl. 92 77305, 1990/92, Mitsui Toatsu Chem. Inc., CA, 1992, v.117, 51883
 92. M. Aritsuka, N. Iwanaga, JP. Appl. 92 77306, 1990/92, Mitsui Toatsu Chem. Inc., CA, 1992, v.117, 51884
 93. P. B. Henderson, C. Coe, T.C. Golden, JP. Appl. 98 259011, 1997/98, Air Products and Chemicals Inc., CA, 1998, v.129, 247238
 94. H. Kasatani, T. Shimada, N. Muranaga, JP. Appl. 96 259206, 1995/96, Japan Pionics, CA, 1997, v.126, 33995
 95. P.B. Henderson, C. Coe, D.E. Foeler, M.S. Benson, US 5069690, 1991, Air Products and Chemicals Inc., CA, 1992, v.116, 50577
 96. H. Harada, H. Momotake, T. Nishitsuji, JP. Appl. 88 306383, 1987/88, Mitsui Toatsu Chem. Inc., CA, 1989, v.111, 117780
 97. H. Hyakutaka, I. Harada, N. Iwanaga, T. Nishitsuji, Appl WO 89 0444 1987/89, Mitsui Toatsu Chem. Inc., CA, 1989, v.111, 216725
 98. H. Yokoma, T. Takumi, F. Mozikawa, JP. Appl. 95 330317, 1994/95, Nissan Chem. Ind. Ltd., CA, 1996, v.124, 180437

99. T. Nagamuze, EP Appl. 807600, 1996/97, Teisan K.K. Japan, CA, 1998, v.128, 36951
100. N. Koto, T. Nishitsuji, N. Iwanaga, I. Harada, EP 344612, 1988/89, Mitsui Toatsu Chem. Inc., CA, 1990, v.112, 80491
101. T.D.Canbria, R.I. Duguid, R. Binder, Proc. - Inst. Environ. Sci.,19992, 38th (vol.1),142-148, CA, 1994, v.120, 248051
102. K. Nakamura, T.Kijima and others, EP 662339, 1994/95, Osaka Santo Kogyo K.K.
103. T. Nishitsuji, H. Momotake, I. Harada, JP. Appl. 88 201007, 1987/88, Mitsui Toatsu Chem. Inc., CA, 1988, v.110,32563
104. J.Chernyakov, T.Hsiao-Ling, A.Schwarz, J.Hsu-Kuang Yang, US 5370779,1996/98, Air Prod. And Chem. Inc., CA, 1998, v.128, 206128
105. Li Yan-en, I.E.Paganessi, D.Vasallo and others, EP Appl. 853970, 1997/98, L'ais Liquide, CA, 1998, v.129, 150742
106. M. Aritsuka, N. Iwanaga, N. Fujeda, JP. Appl. 92114910, 1990/92, Mitsui Toatsu Chem. Inc., CA, CA, 1992, v.117, 93130
107. G. M. Tom, I. V. McManus, W.K. Olander, US 5704965, 194/98, Advanced Technology Materials Inc.,CA, 1998, v.128, 103939
108. G. M. Tom, I. V. McManus, US 5707424, 1996/98, , Advanced Technology Materials Inc.,CA, 1998, v.128, 116684
109. G. M. Tom, I. V. McManus, WO Appl. 96 11739, 1994/96, Atmi Ecosys. Corp., CA, 1996, v.125, 24038
110. H. Ogino, Y. Aomura, T. Suzuki, M.Hatano, Anal. Sci., 1988, v.4, n. 4, 425-426, CA, 1989, v.110, 127698
111. B.A. Mahler, R.N. Miller., WO 99 24358, 1998/99, C.P.C. Kao DuPont, CA, 1999, v. 130, 326793
112. I.M. Grizard, P.Mauvais, Proc. ISSM'96 Int. Symp. Semicond. Manuf. 5th , 1996, 325-28, CA, 1999, v. 130, 75441