

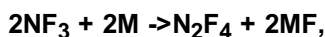
New approaches to nitrogen fluoride synthesis

Message 3

Offer regarding setting of nitrogen fluoride unified production

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Along with the most extensively studied reaction of nitrogen trifluoride with fluorine acceptor:



where *M* – hydrogen, arsenic, carbon, antimony, nitric oxide and other compounds of different classes;

the group of methods, based on oxidization of difluoroamines, the source for which is N,N – difluoro -derivatives of urea, carbamate, mono- or difluoro-derivatives of sulphuric acid, which are obtained by direct fluorination of aqueous solutions of corresponding amides using diluted fluorine at low temperatures, is of practical interest for tetrafluorohydrazine synthesis.

For oxidization of difluoroamines it is offered to use iodine, bromine, aqueous solutions of chromium, iron, cerium, potassium permanganate salts and others. The extraction of difluoroamines out of solutions is necessary to obtain best results regarding yield and fineness of tetrafluorohydrazine in these methods.

This is a serious obstruction for their manufacturing application, because difluoroamines is explosive, especially at changes of phase and that's why they are mainly used for preparative purposes.

The methods, provided for difluoroamines oxidization in the moment of difluoroderivatives extraction directly from N, N solutions are thought to be more perspective.

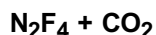
In literature the oxidization of N,N – difluorcarbamate by chrome oxide at 500°N and N, N – difluor-urea by aqueous solutions of such compounds as K₂CrO₄, KMnO₄, CrF₃, Fe(NO₃)₃, Mn₂(SO₄)₃, KFe(SO₄)₂, FeNH₄(C₂O₄)₂, FeNH₄(SO₄)₂, others is described but here there is a number of technological and ecological difficulties, low reproducibility of results.

In the view of technological requirements and economical expediency the most effective scheme for the arrangement of tetrafluorohydrazine production is the following:



The method is based on a cheap, available raw materials, it is not complicated in hardware implementation. The main difficulty of practical implementation of this scheme is the formation of equimolar mixture of tetrafluorohydrazine and carbon dioxide, which separation using physical methods is hardly realized because of closeness of tetrafluorohydrazine boiling point and CO₂ sublimation point (-74,2°N è -78,5°N, respectively) We have studied the opportunity of carbon dioxide elimination in tetrafluorohydrazine using traditional chemical method – coupling the carbon dioxide with aqueous alkali solution.

It is known, that tetrafluorohydrazine, being a strong oxidant energetically reacts with many of organic and non-organic compounds. It is most rational to carry out the dioxide elimination in tetrafluorohydrazine by treatment of



mixture using aqueous alkali solutions at medium temperature and brief contact. The search of such conditions was the aim of the present work. The reactions of carbon dioxide and tetrafluorohydrazine with aqueous solutions of potassium hydrate are studied in a wide range of conditions: temperature range 0 – 80°N, alkali concentration range 5 – 50%, time of contact from 0,5 to 20 seconds in reactors made of glass and stainless steel. The reactor was cylinder, filled with filling and was equipped with casing and fricative bubbler.

It was determined, that the degree of tetrafluorohydrazine decay essentially increases when temperature and alkali concentration increases. For the purposes of illustration picture 1 represents the results of tetrafluorohydrazine interaction with potassium hydrate aqueous solutions at the contact time of 1,2 seconds.

Tetrafluorohydrazine is rather resistant to alkali aqueous solutions at low temperatures in studied conditions. Thus at temperature up to 25°N in 5-30% potassium hydrate aqueous solutions the tetrafluorohydrazine decay doesn't exceed 0,1%. In concentrated alkali (48%) the interaction takes place as early as at 0°N (0,4%), and at 80°N the

tetrafluorohydrazine decay reaches 19,5%.

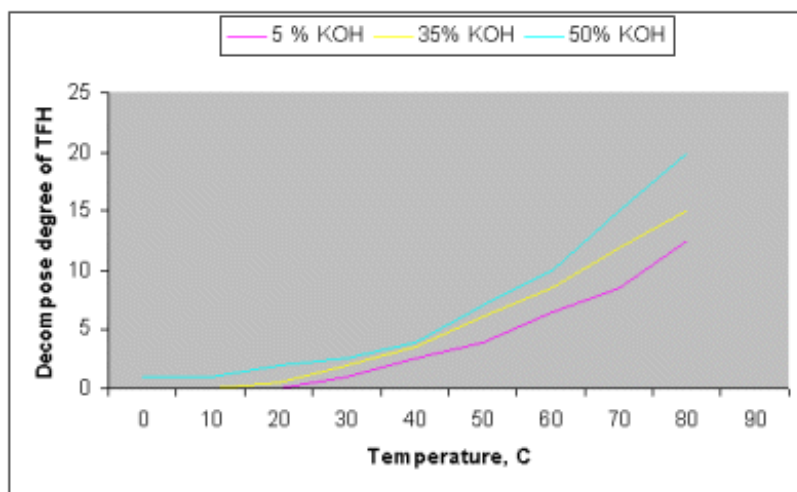
The degree of carbon dioxide absorption was determined at the same conditions. The results are presented at the picture 2. As you can see from data obtained the full absorption of carbon dioxide in 50% solution is reached as early as at 10⁰N, in 30% solution at about 35-40⁰N, and in 5% solution even at 80⁰N the degree of absorption is 99,4%.

Our apprehensions concerning the fact, that during the treatment of tetrafluorohydrazine mixtures with carbon dioxide using aqueous alkali the degree of decay may increase in some way because of local overheating didn't prove to be true. The obtained analysis results allow us to recommend using of potassium hydrate aqueous solutions of 25-35% concentration at 10-25 °C and short term reagents contact for tetrafluorohydrazine. The developed scheme of carbon dioxide elimination in tetrafluorohydrazine essentially simplifies the process of tetrafluorohydrazine obtaining from difluoromines and makes it attractive for detailed technological developmental work and implementation. It was found out before hand that the presence of carbon dioxide doesn't impede the difluoromines oxidization process.

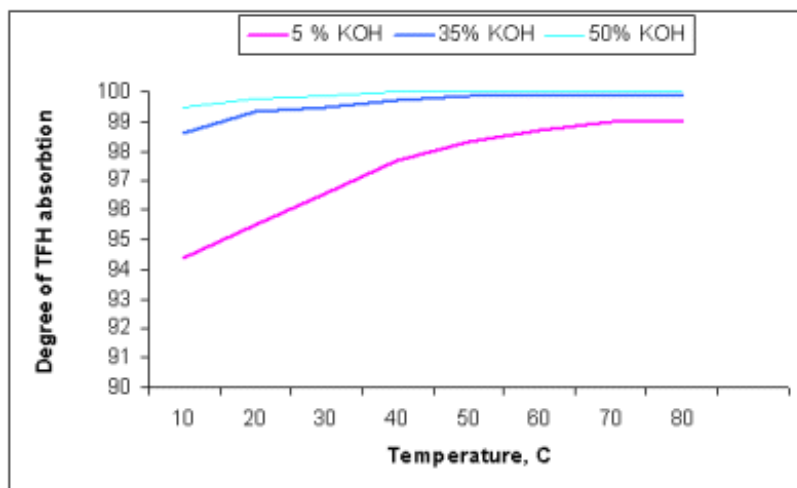
Thus the total scheme of tetrafluorohydrazine obtaining includes the following main steps:

- fluorination of urea's aqueous solution by diluted fluorine at 0-50°C
- acids decomposition of N,N-fluorourea by sulfuric acid at heating
- oxidation of difluoroamine and carbon dioxide mixture by aqueous solution of FeCl₃ without prior purification of difluoroamine
- purification of difluoroamine from CO₂ by KOH
- drying and packaging of tetrafluorohydrazine

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Pic.1 .



Pic.2.

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