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Study and ways of using off-grade propellant Samin unused directly for intended purposes

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Abstract
The fight against pollution of environment with hazardous chemicals turned into one of the global problems of humanity. Such problems include unused reserves of rocket propellants at military warehouses of Azerbaijan after the fall of the Soviet Union. In particular, non-liquid rocket fuel "Samin" used earlier in rocket engines is a dangerous and high-toxic mixture of chemical products. The paper presents the ways and data on utilization of "Samin" to determine possible application fields of the products.

Keywords: "Samin", utilization, xylidine, triethylamine

Introduction
Non-rational use of natural resources causes constant pollution of environment that ultimately leads to the considerable economic losses. On the other hand, all these wastes, for example, chemical wastes are valuable raw materials to produce various substances and reagents for recycling them in industry. For this purpose many countries pay special attention to the recycling process.
Recycling is a method of utilization which results in the processing of waste materials and makes, in our case, chemicals suitable for their recycling in different fields. At the moment one of the examples of negative effect on environment is a forced storage of rocket complexes of non-liquid rocket fuels at warehouses. After the fall of the Soviet Union many military bases were faced different toxic components of rocket fuels which due to long-term storage had been proven to be unsuitable for application and represented a serious threat to environment, and people living in the nearest settlements. These problems arose also because the warehouses with non-liquid fluid rocket fuels decay, corrosion corrodes tanks, and therefore, there is a risk of leakage and ecological catastrophe.
In this connection the task of liquidation and utilization of accumulated off-grade fuel components is an important and topical problem requiring immediate solutions [1-4].

Results and discussion
In the paper [5] we have proposed the utilization method of off-grade nitric-acid oxidizer "Melange"-one of the components of fuel for rocket engines. This paper examines the utilization problems of rocket fuel TG-02 "Samin".
This fuel was previously used as a component in rocket engines. It is highly-inflammable upon contact with "Melange" type oxidizers based on nitric acid with extremely small delay period of auto-ignition. The fuel is hygroscopic, oxidizes by atmospheric oxygen very slowly. The factors catalyzing decomposition process are light, high temperature, humidity and copper ions.
"Samin" belongs to the category of dangerous and toxic products. This fuel may poison in contact with living organism via respiratory tract and skin resulting in headache, dysfunction of the central nervous system and vision disorder.
Our researches have shown that due to gradual depressurization of tanks utilized non-liquid "Samin" become unsuitable by partial change of its chemical composition.
To determine the precise composition "Samin" was distilled for further utilization. It was detected that it contains the mixture of 50-52% technical triethylamine with small quantity of diethylamide and 48-50% of the mixture of technical isomer xylidines and represents a yellow

to dark-brown mobile oily liquid with odor typical for fatty amines. According to toxicological characterization this fuel is referred to the 3rd hazard class (MAC is 3 mg/m^3). During distillation at the range of 89-92^{0}C one of the basic components of the fuel-triethylamine was selected, but the rest mixture was distilled in vacuum (10 mm of mercury) at 76-90^{0}C, since xylidines are distilled under atmospheric pressure at 220^{0}C and partially decompose. The mixture of technical xylidines consists of 6 isomers. The properties and physical and chemical parameters of the fuel "Samin" are given below.

Triethylamine

Tryethylamine is a toxic, colorless low-viscosity fluid with specific amine odor. It is low soluble in water, highly soluble in acetone and is mixed with ethanol.

It may be ignited by heat, sparks or flames. Vapours are heavier than air and form explosive mixtures with air. Contact with triethylamine mainly results in local effects; it can cause severe burns on contact with eyes. Clothing wet with triethylamine will cause skin burns. It is carcinogenic, may result in temporary blue hazy vision, vapours irritate nose, throat, lung, causing coughing, choking and difficult breathing.

Triethylamine can be used in the production of pesticides (simazine, atrazine, cyanazine), corrosion inhibitors (N, N-diethyl urea, dinitrobenzoate, diethylamine), and medicinal substances (novo Caine, codomain) catalysts for synthesis of polyurethanes. Triethylamine is also used to produce wood preservatives, oligomers, stabilizers of trichloroethylene.

Xylidines

Xylidines (dimethy lanilines), mol. 121, 18, are colorless crystals or liquids (see table) with aniline odor, darken rapidly in air. Xylidines are typical aromatic monoamines like aniline. When heated, vapours form explosive mixtures with air. All six isomers are poisonous, causing headache and dizziness and are carcinogenic.

In vacuum distillation 6 isomers with various positions of methyl groups were separated. 3,4-xylidine is a colorless crystalline substance ($t_{melt.}$ 51^{0}C, $t_{boil.}$226^{0}C). The rest xylidines are colorless fluids with unpleasant odor, darken rapidly in air (see tables, 1, 2).

Table 1

	Melting temperature ^{0}C	Boiling temperature 10 mm of mercury
Xylidine 1,2,3	Liquid	89^0
Xylidine 1,2,4	Liquid	79^0
Xylidine 1,2,5	15.5^0	76^0
Xylidine 1,2,6	Liquid	92^0
Xylidine 1,3,4	49^0	96^0
Xylidine 1,3,5	Liquid	92^0

Table 2

Isomer	$T_{melt.}$ ^{0}C	$T_{boil.}$ ^{0}C	d_4^{20}	n_4^{20}
2,3-K	-15	221, 222	0.9931	1.5684
2,3-K (non-symmetrical m-K)	16	214	0.9740	1.5569
2,5-K (n-K)	15.5	213.5	0.9790 (21^{0}C)	1.5591
2,6-K (m-K)	11, 12	216, 217	0.9796	1.5612
3,4-K (non-symmetrical O-K)	51	226	1.0769 (17^{0}C)	1.5612
3,5-k (symmetrical m-K)	9.8	220 221	0.9720	1.5581

All xylidines are highly soluble in ethanol, diethyl alcohol, acetone, chloroform, benzene, and limitedly in water.

Xylidines exhibit the properties of aromatic amines: form salts with mineral acids; with carboxylic acids, their ethers, anhydrides and acid chlorides – N-substituted amides of corresponding acids, with HNO_3 - diazonium salts.

Mixture of isomer xylidines (technical xylidine) comprising 40-60% of 2, 4-xylidine and 10-20% 2, 5-xylidine divides salts by fractional crystallization. For example, 2, 4-xylidine is extracted by processing with 80% of acetic acid with further filtration of acetate and washing with 20% of water solution NaOH. After separating 2,4-isomer 2,5-xylidine is separated in the form of hydrochloride, but 2,4- and 2,5-xylidines used in the production of azo dyes and pigments are the most practically valuable. 2, 6-xylidines are used in the synthesis of pesticides; 3, 4-xylidine – medicinal substances.

Technical xylidine is highly- active additive to aviation petrol, vulcanizing accelerator, antioxidant (for wood material), and foaming agent for ore flotation.

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