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INFLUENCE OF SYNTHETIC FUEL ON NITRILE RUBBERS USED IN AVIATION

Summary. This paper investigates the influence of alternative fuel on selected butadiene–acrylonitrile rubbers used as seals in engine and fuel supply systems of post-Soviet aircrafts. The conventional fuel Jet A-1, the synthetic blending component from hydrotreated esters and fatty acids (HEFA) and its blend were interacted with the sample nitrile rubbers. HEFA technology has been approved by ASTM D7655 for use in turbine aircraft engines. The effect was evaluated on the basis of changes in the nitrile rubber's volume, mass and hardness. It has been confirmed that the synthetic component containing no aromatic hydrocarbons has a different effect on nitrile rubber than the conventional fuel. When the nitrile rubbers were subjected to microscopic observations, the most frequently observed effect was washing out or dissolving of nitrile rubber surface fragments.

1. INTRODUCTION

The continuous development of aviation in recent years [1] has resulted in the perception of this branch of transport also as a significant emitter of harmful substances into the atmosphere. Therefore, the International Air Transport Association (IATA) aimed to reduce CO₂ emission through the adoption of three ambitious targets, including reduction of the total amount of CO₂ emission of the global fleet by half by 2050, compared to the levels of 2005 [2, 3]. One way to achieve this goal is the worldwide use of fuels containing synthetic components [4-6]. Although 10 years have passed since the announcement of these ambitious targets, synthetic fuels are used for the supply of turbine aircraft engines only to a small extent.

The ASTM D7655 [7] standard describes seven accepted technologies for fuel manufacture containing synthetic hydrocarbons for use in turbine aircraft engines:

- Fischer–Tropsch hydroprocessed synthesized paraffinic kerosene (FT SPK);
- Synthesized paraffinic kerosene from hydroprocessed esters and fatty acids (HEFA SPK);
- Synthesized iso-paraffins from hydroprocessed fermented sugars (SIP);
- Synthesized kerosene with aromatics derived by alkylation of light aromatics from nonpetroleum sources (SPK/A) ;
- Alcohol-to-jet synthetic paraffinic kerosene (ATJ SPK);
- Synthesized kerosene from hydrothermal conversion of fatty acid esters and fatty acids (CHJ); and
- Synthesized paraffinic kerosene from hydroprocessed hydrocarbons, esters and fatty acids (HC-HEFA SPK).

These fuels are referred to as "drop-in fuel", i.e., they may be used in engines and fuel supply systems without any modifications [8].

Conventional jet fuel contains a mixture of various hydrocarbons of paraffins (n- and isoparaffins), naphthalenes and aromatics [9]. In such fuels, due to their undesirable properties, i.e. the tendency to form coke deposits on combustor surfaces and to contribute to high-luminosity flames, the content of aromatics is limited to a maximum of 20-25% [V/V] [10]. Moreover, they contain aromatics, which increase the tendency to form soot, which causes the emission of particulate matter [11-13]. Aromatics also contribute to lubricity [14].

In contrast, most synthetic blending components (FT SPK, HEFA SPK, SIP, ATJ SPK, HC-HEFA SPK) practically do not contain any aromatics in their composition [15-17]. Only two of them contain aromatics (SPK/A, CHJ). The aromatics contained in fossil fuel favour the phenomenon of swelling of seals due to the penetration of fuel through the solvent into the solid material and the potential dissolving of one or more components [18]. Because of the reduced number of aromatics in alternative fuels, leakages occur in fuel supply systems [19, 20]. To avoid this phenomenon, a minimum content of aromatic compounds of 8% (V/V) [7] has been introduced. This limit refers to the final blend of jet fuel with synthetic components.

2. LITERATURE SURVEY

Nitrile rubber should be resistant to the interaction of fuels and should not cause any changes in the properties of those fuels. This resistance of nitrile rubber depends on the type of rubber, amount and type of fillers, softeners and vulcanizing unit. Depending on the properties of the fuel and the type of rubber compound, changes in its volume (swelling or shrinkage), mass, hardness, mechanical strength and external appearance may occur.

The nitrile rubber most resistant to liquid fuels is polysulphide nitrile rubber; however, due to its poor mechanical properties and low heat resistance, it is rarely used [21]. The nitrile rubber most commonly used for contact to fuels is acrylonitrile-butadiene rubber (NBR) due to its content of acrylonitrile in the copolymer [22-24], although it is not very resistant to fuels containing aromatic hydrocarbons [25].

The interaction of synthetic fuels with O-ring seals for engine and fuel supply systems in aircraft is of high interest. The propensity of fuels to change the properties of seals is particularly interesting. There is a fear that without the aromatic compounds, synthetic fuels will cause shrinkage, hardening and ineffectiveness of O-rings.

The literature survey was based on studies in which nitrile rubbers used in aircrafts had been subjected to interactions with conventional and synthetic fuels.

Ortner [26], in this study, selected conventional fuels Jet A-1 (aromatics content: 13.7-21.6% [V/V]), synthetic fuels without aromatic compounds and fuels enriched with aromatics by 2, 4, 6 and 8% [V/V]. Different types of nitrile rubber as O-rings used in the aviation industry, i.e.: NBR, fluorosilicone rubber and fluorinated rubber, were subjected to the effects. The following results have been obtained:

- NBR: change in mass and volume decreases with the decrease in the content of aromatics in the fuel, and fuels without aromatics do not have a significant influence on hardness and cracking parameters;
- fluorosilicone rubber: there is a small increase in the mass and volume for all fuels, and hardness decreases if fuels contain the aromatic compounds; and
- fluorocarbon rubber: it remains neutral, and no significant changes have been observed.

Corporan et al. [27] measured the volumetric swelling of nitrile rubber (N0602 – rubber commonly used in aviation) in JP-8 and in six synthetic fuels. The test results are presented in Table 1.

The authors have demonstrated that all fuel components may participate in the swelling process and their impact depends mostly on the strength of the interaction between a specific fuel component and the O-ring, as well as the concentrations of those components in the fuel. They also state that the strength of interaction depends on the molar volume and geometry of the fuel component, polarity and the ability to release hydrogen in the hydrogen bond. In particular, volumetric swelling tends to increase when the molar volume of the fuel component decreases and polarity and hydrogen bonds

increase. In case of alternative fuels, their components have very low polarity and little, if any, ability to form even weak hydrogen bonds, leaving only the molar volume and geometry as the main mechanism to induce volume swelling in the O-ring.

Table 1

Volume swell of nitrile rubber

Fuel	Volume change [%]
Shell FT (Fischer-Trposch)	9,6
Sasol FT	9,5
Rentech FT	7,8
R-8	7,0
Camelina RHJ	9,1
Tallow HRJ	8,6
JP-8 (conventional jet fuel)	16,6

Link et al. [28] have conducted swelling tests of nitrile rubber (N0602-70), interacted with conventional fuel for turbine aircraft engines, conventional diesel fuel and their synthetic equivalents. The test results are presented in Table 2.

Table 2

Volume changes of nitrile rubber O-rings

Fuel	Volume change [%]
Conventional jet fuel (JP-5)	16,2±1,0
Conventional Diesel	14.0±0,6
Synthetic jet fuel (S-5)	0.7±0,2
Synthetic diesel	-0,7±0,3

Studies have revealed that it is possible to adjust swelling of the sealing O-rings in turbine aircraft engines by enriching the fuel with certain additives. On the basis of calculation modelling of the energy of interaction between the nitrile rubber monomer and various chemical substances, the authors found that substances with the potential for double interaction, one with the polar nitrile group and the other with the electrons in the butadiene system, will provide the highest degree of swelling.

Graham et al. per [29] have also discussed the swelling of nitrile rubber (N-602-70-214) under the influence of JP-5 (conventional and synthetic). They found that aromatic hydrocarbons in fuels caused swelling of nitrile rubber. Moreover, therein, the tendency of nitrile rubber to swell increases with the polarization and hydrogen bond of aromatic compounds. This effect suggests that swelling of nitrile rubber requires interruption of attractive forces between cyanide groups on adjacent polymer chains and their replacement with interactions of the cyanide group with the aromatic. It has also been found that volumetric swelling decreases with an increase of the molecular weight.

The effects of the type and concentration of aromatic solvent (Aromatic 100, 150 and 200) on the swelling characteristics of rubbers, i.e. nitrile rubber (N0602), fluorosilicone rubber (L1120) and fluorocarbon rubber (V0747), have been tested by DeWitt et al. [30]. The tests were carried out on synthetic fuel obtained according to the Fischer–Tropsch (FT) method that had been blended with additives used in conventional jet fuels and aromatic solvents at various concentrations – 5, 10, 15, 20 and 25% (the range of aromatics found in typical fuels). In the case of nitrile rubber, the significant increase in volume was strongly influenced by hydrogen bondings, polarity and molar volume. The

authors have also stated that general swelling strongly depends on the naphthalene content in the fuel. In the case of fluorosilicone, all blends (FT/aromatics) caused swelling in the typical range for JP-8. This indicates that that material is weakly affected by polarity and hydrogen bonding, but is, above all, affected by molar volume. The volumetric swelling of fluorocarbon rubber was slightly higher in the case of blends than in the case of JP-8, but the absolute difference was minimal. The authors have also stated that volumetric swelling is linearly dependent on the total concentration of aromatic solvents and its type for all tested materials. The tendency towards volumetric swelling is attributed to a decrease in molar volume and increased potential for polarization and hydrogen bonds.

Literature review, contains fuels and rubbers types was used in research, is presented in Table 3.

Table 3

Literature review [26-30]

Rubber	Fuel					
	Fossil jet fuel		FT SPK*	HEFA SPK*	ATJ SPK*	Synthetic fuel* with aromatic compounds
	military	civil				
Nitrile (NBR)	[27-29]	[26], [28]	[26-30]	[26], [27]	[26]	[26], [30]
Fluorosilicone		[26]	[26], [30]	[26]	[26]	[26], [30]
Fluorocarbon		[26]	[26], [30]	[26]	[26]	[26], [30]

*fuels described in ASTM D7655

The above research presents the influence of synthetic fuels on different rubbers (produced according SAE International standards), which are used only in major aircraft engine and airplane manufacture and are resistant on jet fuels such as Jet A-1, Jet A, F-34 and JP-8. For this reason, the authors decided to select nitrile rubbers used in post-Soviet aircrafts (produced according to the TU specification), which are resistant to jet fuels commonly used in the Commonwealth of Independent States e.g. T-1 or TS-1. This research can be useful in the certification of post-Soviet platforms on synthetic jet fuels.

3. MATERIALS AND METHODS

The nitrile rubbers listed in Table 4, which are used in post-Soviet aircrafts, have been selected for this study. These rubbers are used in fuel supply systems and engines in helicopters as well as fighters exploited by the Polish Armed Forces.

The following fuels have been used for testing the influence on nitrile rubber:

- conventional jet fuel – Jet A-1 (designation Jet A-1);
- synthetic blending component from HEFA technology, feedstock UCO – used cooking oil (designation UCO); and
- blend of Jet A-1 with synthetic blending component in a proportion of 50/50% [V/V] (designation 50%UCO).

The HEFA blending component and its blend with fossil jet fuel was selected, due to the increasing use of synthetic fuels in civil and military aviation. The properties of fuel samples are presented in Table 5.

The requirements for Jet A-1 are specified in the ASTM D1655 standard, and for the synthetic component and its blends with Jet A-1 in ASTM D7566. In the range of tested parameters, the properties of UCO differ from Jet A-1. The synthetic blending component is characterized by lower density and higher viscosity, calorific value and flash point in comparison to Jet A-1. The highest difference between fuels is in the content of aromatics.

Table 4

Classification of nitrile rubber selected for tests according to type, operating conditions and application [31]

Rubber No.	Rubber group	Type	Operating conditions		Application
			Medium	Temperature [°C]	
IRP-1078	Gasoline- and oil-resistant rubbers based on nitrile rubber	SKN-18 + SKN-26 (acrylonitrile-butadiene)	fuels: T-1, TS-1, T-6 AMG-10 oil	-50 ÷ +150	parts for movable and fixed connections working under static deformation
NO-68-1		SKN-18 + nairite (acrylonitrile-butadiene)	fuels: T-1, TS-1 oils: MK-8, MS-20	-55 ÷ +100	parts for movable and fixed connections working under static deformation
3825		SKN-40 (acrylonitrile-butadiene)	fuels: T-1, TS-1 oils: MK-8, MS-20	-30 ÷ +100	parts working under static deformation
3826s		SKN-40 (acrylonitrile-butadiene)	fuels: T-1, TS-1 AMG-8 oil	-40 ÷ +100	
4327		-	SKN-18 + SKN-26 + polysulphide rubber (acrylonitrile-butadiene + polysulphide)	fuels: T-1, TS-1 transformer oil	-55 ÷ +100

To determine the influence of prepared fuels on selected nitrile rubbers, the following were carried out:

- tests of nitrile rubbers properties according to PN-C-40005 in varying ranges of
 - volume;
 - mass; and
 - hardness.
- observation with an optical microscope.

The following conditions of fuel interaction with nitrile rubbers were selected:

- interaction time – 72 h (3 days);
- temperature – 70°C;
- amount of test fuel in the glass vessel – 100 ml;
- tightly sealed fuel vessel; and
- dimension of the nitrile rubbers: 15x15 mm.

Table 5

Properties of tested fuels

Property	Unit	Test method	Results		
			Jet A-1	50%UCO	UCO
Density at 15 °C	[kg/m ³]	ASTM D4052	789,3	770,7	751,9
Viscosity at -20 °C	[mm ² /s]	ASTM D445	2,998	3,481	4,077
Viscosity at -40 °C	[mm ² /s]	ASTM D445	5,479	6,633	8,202
Net heat of combustion	[MJ/kg]	ASTM D3338	43,312	43,741	44,172
Aromatics	[% (V/V)]	ASTM D1319	15,1	7,2	-
Flash point	[°C]	ASTM D56	41,5	42,5	43,0

4. RESULTS AND DISCUSSION

4.1. Properties of nitrile rubbers

The results of tests for fuel samples on nitrile rubbers are shown in Figs. 1 – 3.

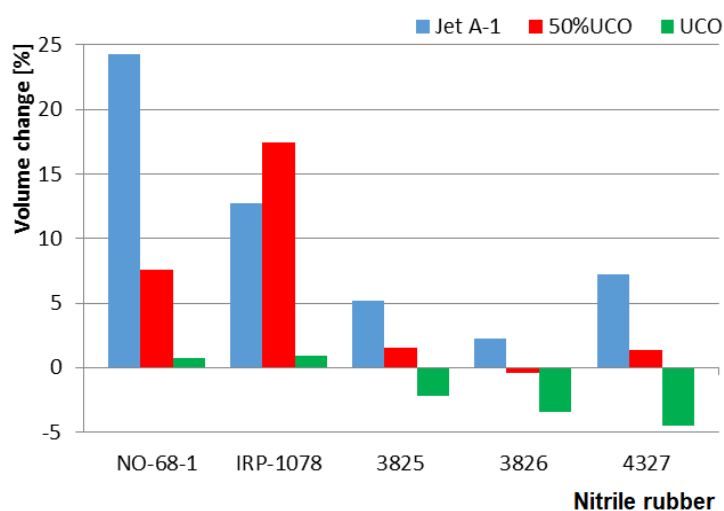


Fig. 1. Volume change of nitrile rubbers

The conventional fuel in nitrile rubbers causes their swelling. This is mostly visible for rubber NO-68-1 (increase of volume by approx. 25%). Introduction of a synthetic component into Jet A-1 changes the characteristics of rubbers – smaller volume changes have been observed than those for Jet A-1 (except for rubber IPR1078). Moreover, the interaction of nitrile rubbers with UCO causes a slight increase in volume or even shrinkage, which may translate into leaks in distribution fuel supply systems.

Introduction of UCO into fossil fuel also affects the change of nitrile rubbers mass (Fig. 2). The interaction of Jet A-1 and nitrile rubbers increases their mass, while UCO causes the opposite trend – decrease of mass of all tested nitrile rubbers. The mass change after interaction with a fuel with no aromatic hydrocarbons may indicate the extraction of additives (e.g. plasticizer, antioxidants).

The realized tests allow the conclusion that the hardness of nitrile rubbers decreases when exposed to Jet A-1. The highest hardness changes have been obtained for nitrile rubber 4327, amounting to approx. 25%. Furthermore, the aromatic hydrocarbons contained in conventional fuel are dispersed in

the material and take over the role of plasticizers. The UCO with no aromatics slightly reduces the hardness of some nitrile rubbers, and in two cases, even increases it. That phenomenon is most likely caused by the fact that saturated hydrocarbons, which are the main constituent of synthetic components, have much lower tendency to diffuse.

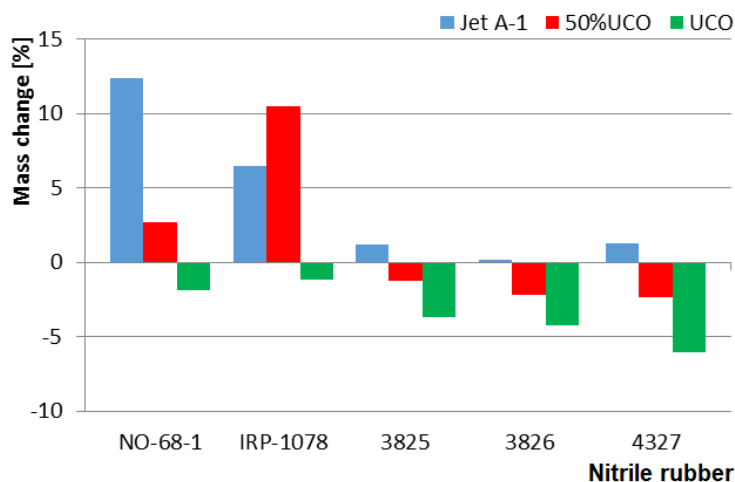


Fig. 2. Mass change of nitrile rubbers

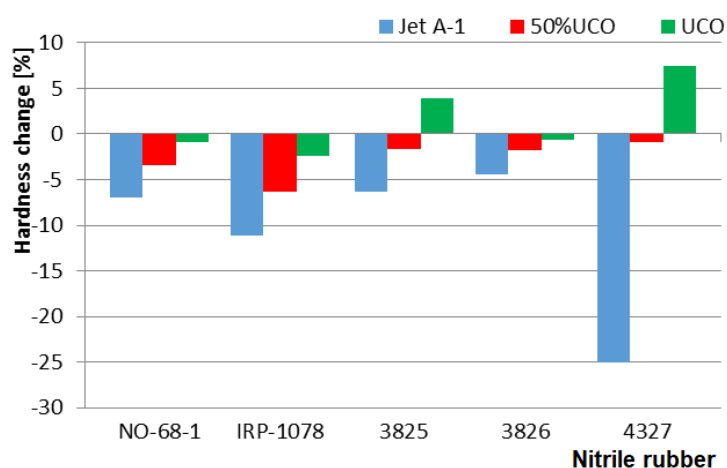


Fig. 3. Hardness change of nitrile rubbers

4.2. Observation with an optical microscope

Below, selected photos of the surface condition of selected nitrile rubber are presented. The images have been taken using a Nikon Eclipse LV100ND optical microscope with a Nikon DS-Ri2i camera and NIS-Elements BR software using bright-field (BF) technology, magnification 10x20 - scale of 100 μm . The presented images are related to the influence of fuel samples on nitrile rubbers. The initial surface refers to the condition of nitrile rubber surface not affected by the fuel. The nitrile rubbers were described on the basis of selected photos/microphotographs.

In general, the surfaces of selected nitrile rubbers are not homogeneous before fuel interaction. These are probably fragmenting of fillers exposed to the atmosphere (oxidized). Interaction with fuel samples usually results in the removal (washing out) of parts of those objects.

On comparing the interaction of the Jet A-1 fuel and UCO with nitrile rubber 3825, it is found that UCO interacts more aggressively/intensively than Jet A-1. In both cases, the remains of the surface layer have the nature of etched dendritic structures (polycrystals) – probably nitrile rubber fillers.

The interaction of Jet A-1 (Fig. 4b) results in 70-80% of all objects (fillers) being washed out of the surface layer. The characteristic dendritic structures of crystals size < 100 μm have remained.

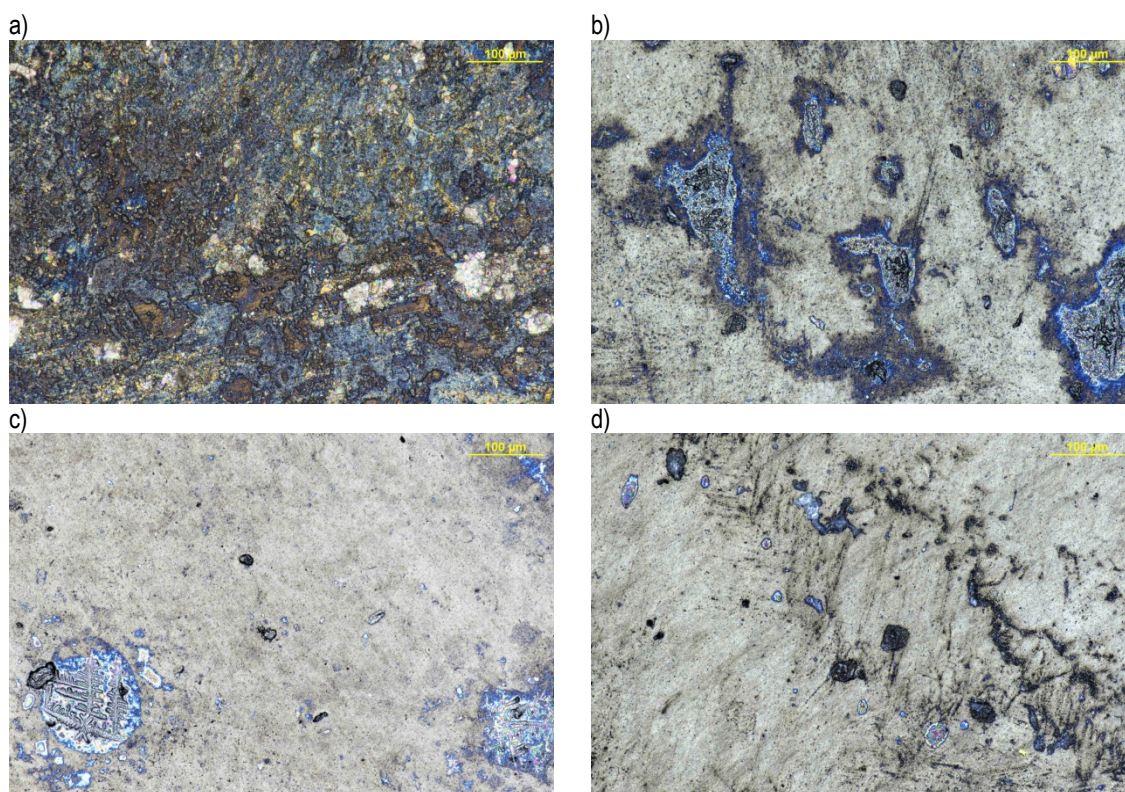


Fig. 4. Nitrile rubber 3825: a) initial surface, b) Jet A-1, c) 50%UCO and d) UCO

The addition of UCO to Jet A-1 (Fig. 4c) results in a more intensive fuel impact. Approximately 80-90% of the nitrile rubber surface layer has been washed out; the characteristic dendritic structures of crystals $< 100 \mu\text{m}$ remained.

The interaction of UCO (Fig. 4d) results in the loss of approx. 90% of the nitrile rubber surface layer. The characteristic dendritic structures of crystal size $< 50 \mu\text{m}$ have remained.

On the surface of nitrile rubber 3826s not exposed to fuels (Fig. 5a), numerous crystalline structures up to $30 \mu\text{m}$ can be seen. There are no significant changes in the surface after the interaction with Jet A-1 (Fig. 5b). The influence of 50%UCO (Fig. 5c) and UCO (Fig. 5d) results in a slight decrease in the number of crystallites - by approx. 30-40%. Also, small ($< 30 \mu\text{m}$) irregular secretions on the surface of the 3826s compound have appeared.

Investigation of fuel samples' interaction on nitrile rubber 4327 shows that no significant changes have been found in the microscopic image (Fig. 6). On the surface of elements subjected to interaction fuels, only a few, flat separations of $200\text{-}300 \mu\text{m}$ have been observed (Figs. 6b, c, d).

The nitrile rubber JRP 1078 interacts with the fuels. The surface before tests is heterogeneous (Fig. 7a) and dark grey in colour. There are needle-shaped crystallites with a length $< 50 \mu\text{m}$ evenly distributed over the surface. The impact of Jet A-1, 50%UCO and UCO fuels on the JRP 1078 surface is similar (Figs. 7b, c, d). The needle-shaped crystallites present on the untested rubber surface were removed in all examined cases (Figs. 7b, c, d).

The nitrile rubber NO-68-1 interacts with the fuel, but only to a small extent. The surface characteristic of nitrile rubber interacting with fuels is similar to that of the initial surface. There is a clear loss of crystallites/filler particles after fuel interaction. The influence of UCO and 50%UCO is slightly more aggressive.

The influence of Jet A-1 (Fig. 8b) results in washing out of approx. 50% of all crystallites of size up to $30 \mu\text{m}$ (as compared to Fig. 8a). Use of 50%UCO (Fig. 8c) results in the removal of approx. 60-70% fewer crystallites in relation to the initial surface. A similar picture has been obtained for the surface of nitrile rubber NO-68-1 treated with UCO (Fig. 8d). The loss of about 60-70% of crystallites in relation to the initial surface has also been found.

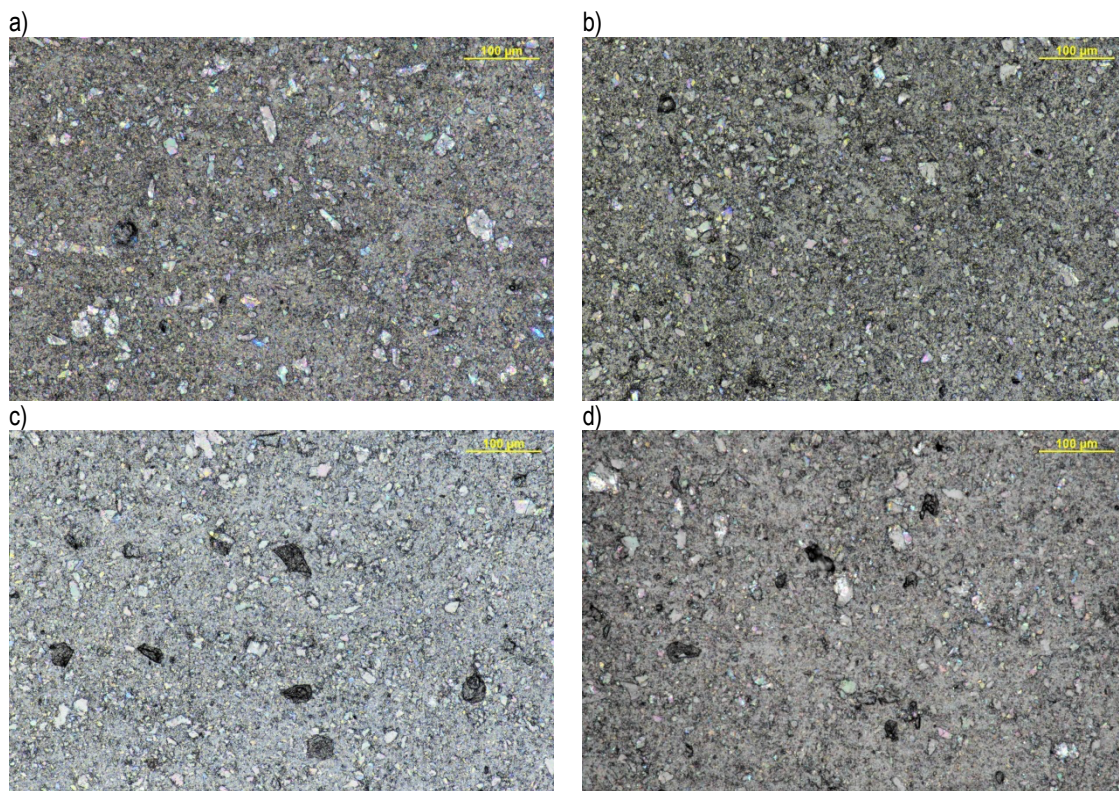


Fig. 5. Nitrile rubber 3826s: a) initial surface, b) Jet A-1, c) 50%UCO and d) UCO

The microscopic observation can be summarized as follows:

1. The tested nitrile rubbers interact with the fuel samples. This is visible in the image of rubbers' the surface.
2. Usually, it is the effect of washing out or dissolving fragments of the surface layer (in fact, objects on the surface).
3. The effect of changes on the surface may be visible (but not necessarily) in contamination of fuel (not necessarily in the form of a separate phase), and in changes in mechanical properties.
4. In the case of nitrile rubbers 3825, 3826s and NO-68-1, more intensive interaction of UCO has been observed.

5. CONCLUSIONS

This paper presents the influence of synthetic fuels on selected nitrile rubbers used in aviation. The synthetic blending component was obtained from HEFA technology. Several types of nitrile rubber used in fuel supply systems and engines of post-Soviet aircrafts have been investigated. Tests of nitrile rubbers' properties to determine changes in volume, mass and hardness have been realized. The following conditions of tests have been assumed: temperature of 70°C and time course of 72 hours. Observations with an optical microscope were also made.

Introduction of a synthetic component into Jet A-1 changes the characteristics of rubbers. Smaller volume changes have been observed for 50%UCO and UCO than for Jet A-1 (except for rubber IPR1078). The interaction of nitrile rubbers with UCO causes a slight increase in volume or even shrinkage. Jet A-1 causes increases in the mass of nitrile rubbers, while UCO causes the opposite trend - decrease of mass of all tested rubbers. Hardness of nitrile rubbers decreases when exposed to Jet A-1 (e.g. nitrile rubber 4327 by approximately 25%). Changes in rubber hardness for 50%UCO and UCO are generally smaller than that for Jet A-1.

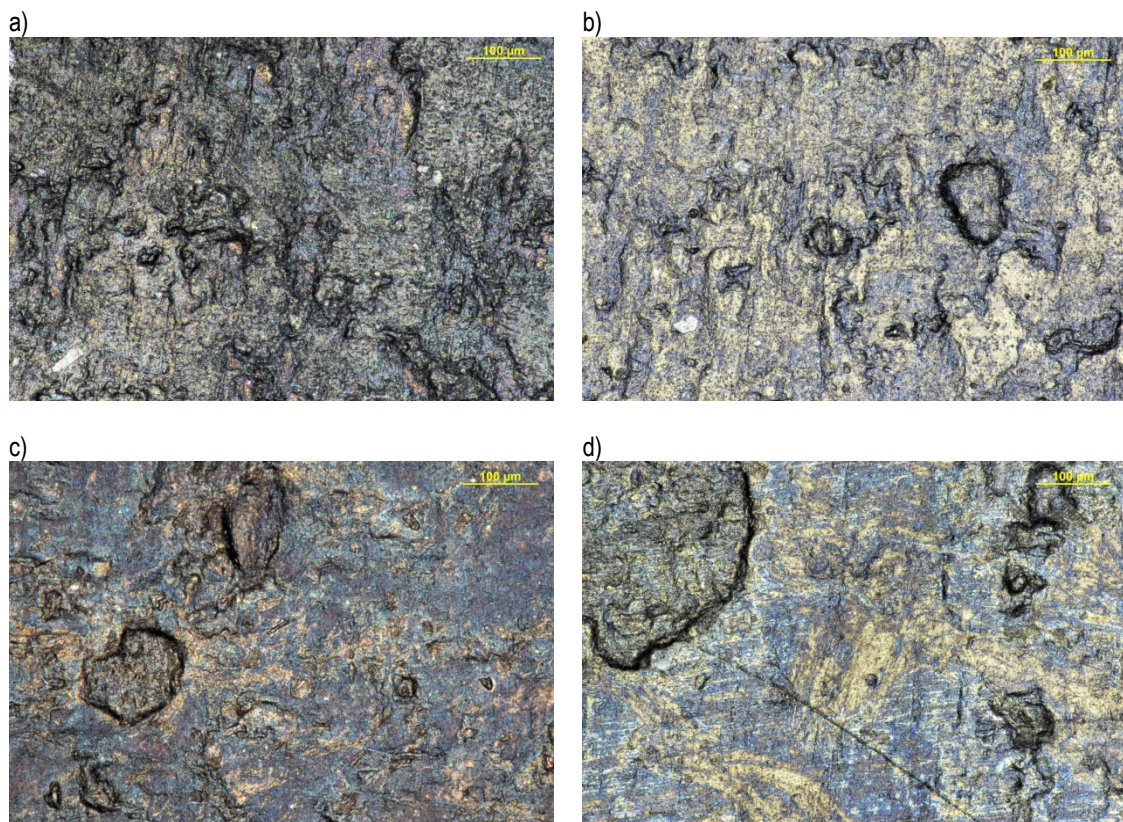


Fig. 6. Nitrile rubber 4327: a) initial surface, b) Jet A-1, c) 50%UCO and d) UCO

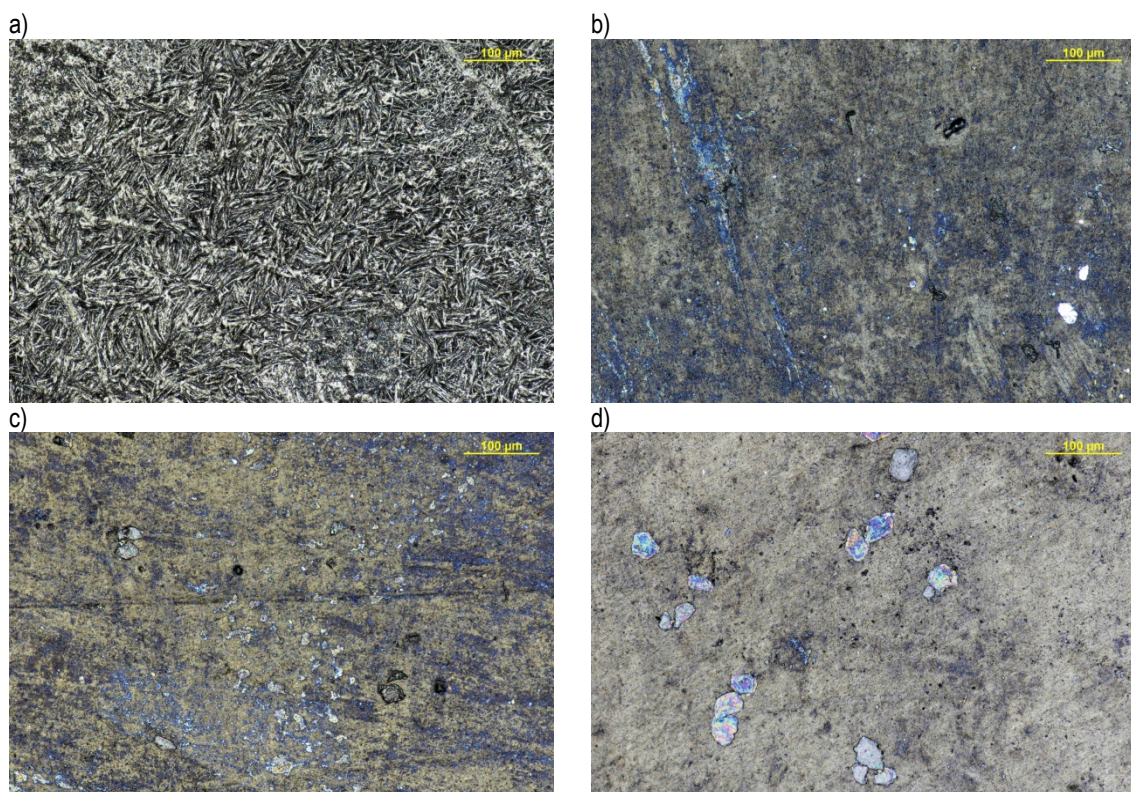


Fig. 7. Nitrile rubber IRP-1078: a) initial surface, b) Jet A-1, c) 50%UCO and d) UCO

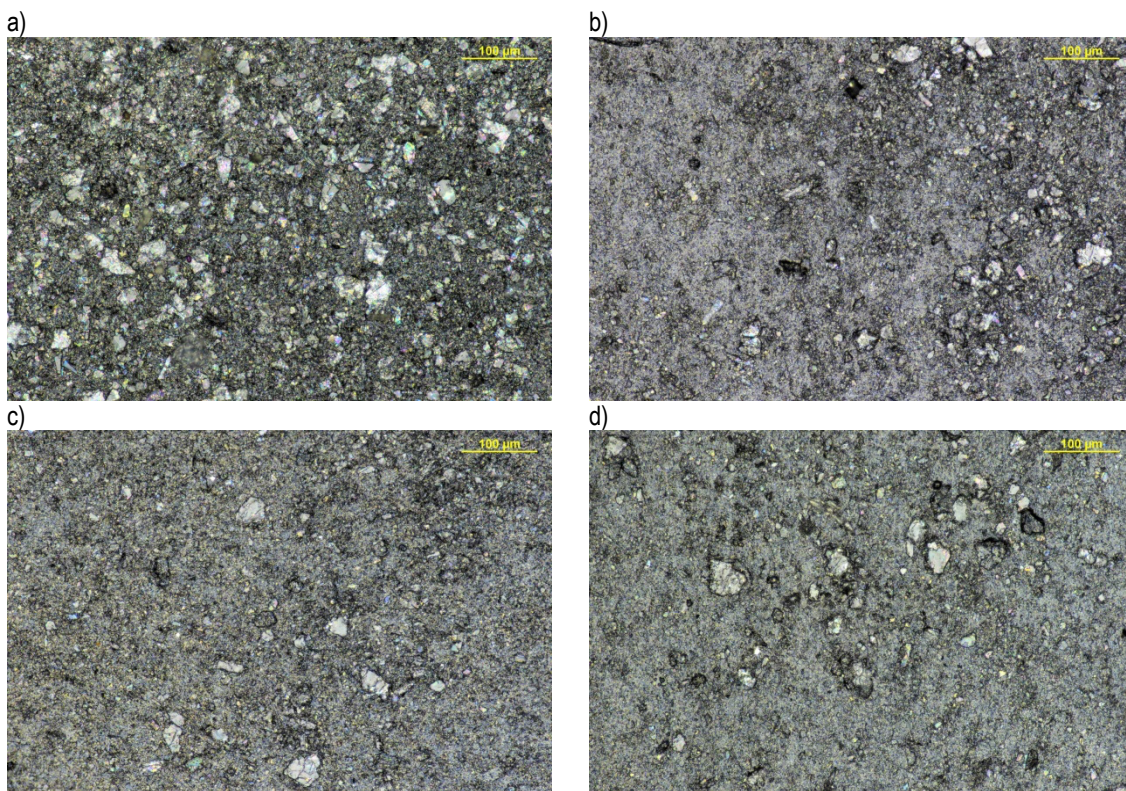


Fig. 8. Nitrile rubber NO-68-1: a) initial surface, b) Jet A-1, c) 50%UCO and d) UCO

Interactions of nitrile rubber with Jet A-1 cause a volumetric increase (sealing function), whereas UCO, which does not contain aromatic compounds, does not induce this phenomenon. It should be noted, however, that in aircraft turbine engines, fuel with a component content of up to 50% is allowed to be used, while maintaining the minimum content of aromatic compounds, i.e. 8%, which guarantees proper swelling of nitrile rubber in the systems.

In the microscopic studies, the influence of fuels on nitrile rubber has also been observed. The most frequently observed effect was washing out or dissolving of fragments of their surface layer.

Further research in this area, including all rubbers found in post-Soviet aircrafts, will be useful in the certification of aviation platforms on synthetic jet fuels.

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