SECURITY DIMENSIONS
INTERNATIONAL & NATIONAL STUDIES
NO. 21; 2017 (62–74)
DOI 10.24356/SD/21/3

SPECIFICITY OF LEAKING NITRIC ACID FROM A TANK VEHICLE

ING. MICHAL ORINČÁK, PH.D.
Žilinská Univerzita, Slovakia

PROF. ING. JANA MÜLLEROVÁ, PH.D.
Žilinská Univerzita, Slovakia

ABSTRACT

The paper deals with the leakage of nitric acid in road transport (ADR); its specifications, problems and complications during its leakage from the tank into the environment. The first part describes specific characteristics and their means of transport. Following part discusses the experimental investigation of the specific characteristics of HNO_3. The experiments on reaction of nitric acid in contact with diesel, gasoline, valvoline engine oil and coolant as well as with samples of common vehicle's materials such as iron, aluminium, copper, tire rubber, ABS plastic and asphalt. Reactions observed not always met the expectations of strong reactions as described in Security data sheet. The third part describes a possible ways of acid leakage from the tank and its disposal. Recommendation concerning effective action of Fire units are described in order to stop the leaking and minimize the damage caused by nitric acid.

ARTICLE INFO

Article history
Received: 08.02.2017 Accepted 28.02.2017

Key words
nitric acid, leak, tank, road transport, experiment, metal, asphalt, rubber

INTRODUCTION

Transport of dangerous goods includes within the so-called. "Special transports" that include objects and substances requiring transport in

terms of non-standard conditions (eg. Packaging, handling, construction vehicle, etc.). This issue is currently addressed by ADR (European Agreement concerning the International Carriage of Dangerous Goods)[1].

In the national transport of dangerous goods it has been adopted with effect from 19th 1996 Act. 168/1996 Coll. The agreement defined the class of dangerous substances according to their characteristics, determine the conditions for their transport, packaging, marking, rules for use and filling out the required documents. It also defines requirements for vehicles including technical requirements for vehicle according to each class, limiting the amount of transported goods, supervision, by public and parking[2]. The top of the listed Kemler code that indicates imminent danger and at the bottom of the rectangle is given an identification number of the substance, which we call the UN code. UN code is characterized by four digits that is associated today about 3 000 substances and mixtures of the substance or mixture is identified. If there are multiple shipments of dangerous goods, the vehicle is labelled at the front and rear and clean orange plates on each side of the eventual tank compartment is a separate table with orange Kemler[3] and UN code and marking[4].

Transportation of dangerous goods by road network is carried in tanks or tankers of different sizes, which must be made of materials according to prescribed standards, to be able to withstand the effects of dangerous substances. For the carriage of nitric acid are commonly used aluminium tanks with shells and recently began using tanks from corrosion resistant steel Nicrofer 3127 HMO – 31 alloy material rustproof tanks acid at normal temperatures reliably resists and has sufficient strength and high resistance to puncture even if accident. An important part of tanks shall be breakwaters, whose main function is to prevent the spill-free fluid transported and its subsequent impact to the head tank[5].

[1] A. Čajda, *Bezpečne s nebezpečnými vecami*, Bratislava 2015, p. 27.

[2] J. Došek, J.Kokeš, *ADR*, Praha 2007, p. 46–50.

[3] Karta bezpečnostných údajov, Ministerstvo hospodárstva Slovenskej republiky, http://www.economy.gov.sk/kartabezpecnostnych-udajov/142568s (accessed: 11.03.2016), p. 1–3.

[4] Kemler a UN – označování nebezpečných látek při silniční přepravě, p. 3–4.

[5] Sbor dobrovolných hasičů Praha – Zličín: Identifikace nebezpečných látek – Kemler kód, p. 2.

Nitric acid is most often used for the production of fertilizers, explosives, etching, and metal dissolution. As component aqua regia is also used for the cleaning and extraction of gold, and the synthesis of chemicals. Nitric acid is a strong oxidizing agent. Reacts with cyanides, carbides and powdered metals can take place explosively. The reactions of certain organic substances, e.g. turpentine, are violent and pyrophoric. Concentrated nitric acid stains human skin, yellow (reaction with keratin). Nitric acid is unstable in air and light, further extends the russet toxic gaseous carbon dioxide, therefore, kept in bottles of dark glass and double seal. The most commonly produced by reacting nitrogen dioxide with water or hydrogen peroxide.

Specific properties of nitric acid includes in particular its ability to support the fire particularly when reacting with oxygen and organic compounds. It represents a strong oxidizing agent. Nitric acid causes severe burns and skin damage. Its vapours are corrosive and irritating effects on eyes and respiratory system. As the acid changes the pH of the water it has a detrimental effect on water organisms[6].

The domestic transport (within the country) is considerably more frequent than international transport. There was transported about 310 000 tons of hazardous substances per year in the period 2010 – 2012 in average[7]. The most often transported dangerous substances in Slovakia are flammable liquids, flammable solids, and gases.

Most Likely Reasons of Nitric Acid Tank Leakage

The most common reasons of nitric acid tank leakage are following:
– Loss of tightness of seal valves and tank shell (ie. Tearing, spills and so on.),
– Puncture of the tank shell,
– Use of improper tanks,
– Operator error during filling or refilling the tank contents.

Loss of tightness in particular drain valve are amongst the most emerging leaks of hazardous substances that tend mostly to 100 liters. Such leakage is easier to stop the spill and disposal, as for the leakage that is caused by piercing the tank, e.g. in a traffic accident. In transfer-

[6] Bezpečnostní listy, Penta, p. 3.

[7] Ročenka dopravy a telekomunikácií 2013, Štatistický úrad Slovenskej republiky, 2014, p. 128–132.

ring the tank it leads to a situation where the sealing cracks very complex and usually there is a leakage of the substance. Improper use tanks selected substances can be classified leaks that occur in our country rarely (mostly foreign carriers concerned). The situation, when used the wrong kind of tanks of nitric acid and was a leak arose in 2010 in the Orava region, where the E77 road in the direction of the village to the city wide Dolny Kubin leaked nitric acid through a crack in the shell of the tank. Also not forgetting the risk of possible leakage of corrosive in its filling or refilling.

Experiments on Reactivity of HNO_3 with Common Materials

Nitric acid is characterized by its specific properties under the reaction substances contained in the area. When the carriage by road network are particularly fuel, fluids and materials transport unit (eg. A tractor tanker semi-trailers), with which it can respond to uncontrolled and thus complicate the procedure itself of its liquidation. When the experiments carried out with nitric acid, we chose fuels and materials that when transporting occur most frequently.

Samples of materials:

– Metal – iron,
– Metal – aluminium,
– Metal – copper,
– Rubber – tire
– ABS plastic,
– Asphalt.

Samples of fuel (fuel):

– Diesel,
– Natural gas 95,
– Valvoline engine oil 10W-40,
– Coolant G11.

Studied experimental parameters:

a) measurement of temperature and pH, of the material,
b) The degree of destruction of the material of the reaction,
c) Water absorption of the material, e.g. in rubber, plastics and metals is more of smoothness and porosity of the surface of the sample material, which affects the capture of liquid on its surface (build-up).

The degree of destruction of the material:
0 without visible damage,
1 damage is visible microscope,
2 damage is visible by the eye,
3 Severe destruction of the material.
The degree of the reaction:
0 No reaction,
1 weak reaction without visible symptoms,
2 quick response to visible manifestation,
3 uncontrollable, violent reaction.

Figure1 Samples of oil, diesel, gasoline and coolant

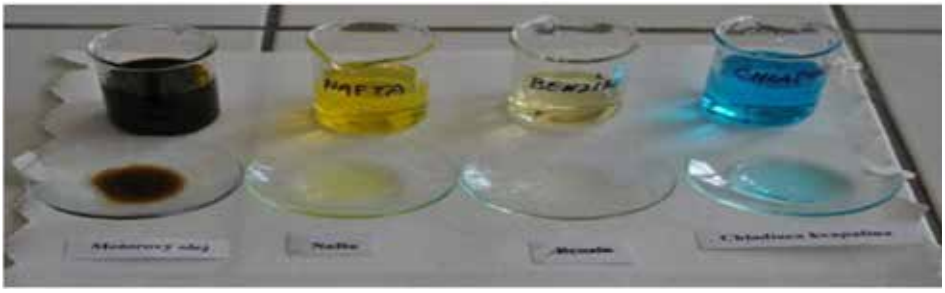
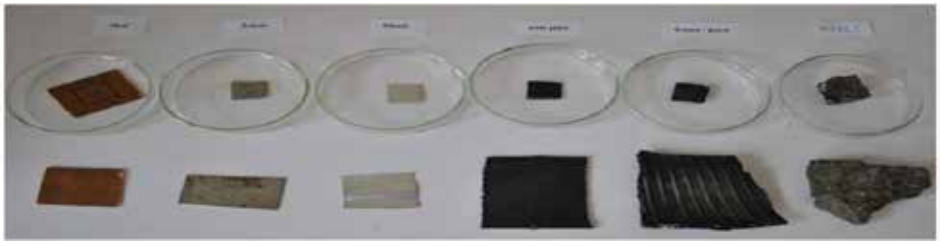


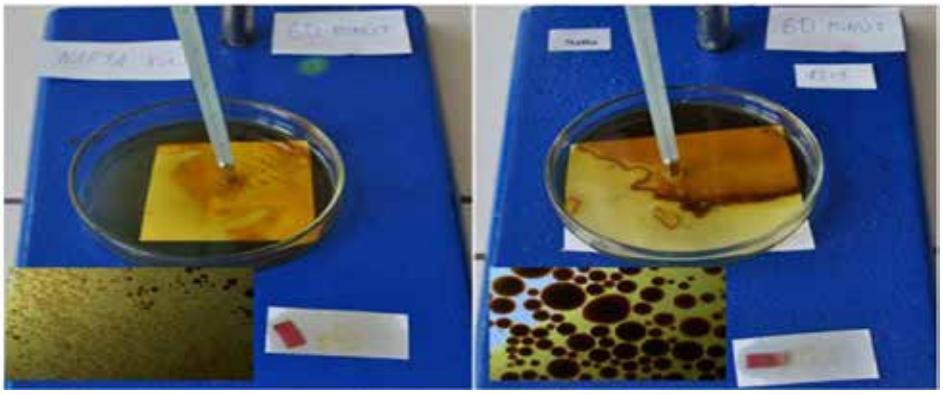
Figure 2 Samples of materials (copper, steel, aluminium, ABS plastic, tire-rubber, asphalt) prepared for experiment



Nitric acid solution (65%) in amount of 2 ml was applied in the each sample of fuel, fluids (Fig.1). and solid materials (Fig.2). In the case of a fuel tank and fluid that was a 1: 1 and 1: 5 (5 parts by fuel and 1 part HNO_3), and the oil was still a ratio of 13: 1 (13 parts of oil, and 1 part HNO_3). Subsequently, the changes in temperature and pH of the solution as well as the reaction were tracked.

Oil and acid reaction was calm. In a 1: 1 there is a change of color oil which turned white, and the reaction was visible border between the oil and acid. 30 minutes after exposure to diesel changed its density was visibly less dense (loose). In the reaction of 5: 1 a precipitate formed, which in a ratio of 13: 1 was clear and darker. It was confirmed that the greater quantity of oil, at fig. 5.

Figure 3 Microscopic images of the sample of diesel with HNO_3 in a ratio of 5:1 and 13:1 after 60 minutes



The reaction of the gasoline and nitric acid in a ratio of 1: 1 was carried out without major changes and reactions, see. Figure 6 and Table 2. There was only a change in the color of gasoline. It became pale and the clear boundary between gasoline and acid was visible. There has thus merging them. In a test at a ratio of 5: 1 (5 parts of gasoline and 1 part acid) solution of gasoline and acid the yellow colour was visible. For both reactions, there was a small increase in temperature, but this was due to the influence of the external environment.

Table 1. Experimentally observed reactions of HNO_3 and common materials from April 2016

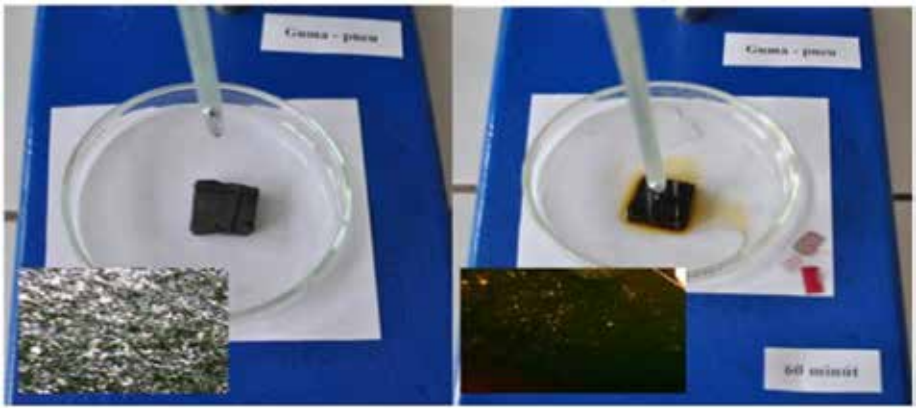
Reactant type	Duration (min.)	ph (HNO_3+-reactant)	Δtemp.	Destruction level (0–3)	Reaction level (0–3)	Observation
diesel (93:7)	15	0.5	0.75	-	1–2	Local coagulation created
	30	0.7	0.75	-	1–2	Local coagulation created
	60	1.7	1.0	-	2	Dark dense coagulation
gasoline (50:50)	15	1	0	-	1	Gasoline colour changed to white; visible boundary between reactants – substances not allied
	60	1	0	-	1	Gasoline colour changed to white; visible boundary between reactants – substances not allied
Valvoline engine oil	60	-	-	-	1	The oil dense became lower, the colour changed to lighter
COOLANT	60	-	-	-	1	Coolant collour changed to light-blue
Tire Rubber	15	0.2	0	1–2	1–2	Solution changed colour to dark brown; rubber is softer and soaky,

	30	0.4	0	1–2	1–2	Solution changed colour to dark brown; rubber is softer and soaky,
	60	1.1	0	1–2	1–2	Solution changed colour to dark brown; rubber is softer and soaky,
STEEL	30	-	-	1	1	Calm reaction, no changes visible
	60	-	-	1	1	Calm reaction, no changes visible
	90	-	-	3	3	Sudden very strong reaction, irritative gases of NOx released
CoPPER	15	-	-	3	3	Very strong reaction, irritative gases of NOx released
ASPHALT	15	-	-	2	2	Asphalt became sophter and easy to scratch
ABS PLASTIC	90	-	-	1	1	Calm reaction, microscopic changes observed
AlluminIum	90	-	-	1	1	Calm reaction, microscopic changes observed

Figure 4 Gasoline sample before the experiment, and with HNO_3 in a ratio of 1:1 at 60 minutes and microscopic images

Reaction of rubber (tire) with nitric acid was carried out quickly with visible signs of its effects on the sample (Fig. 5) as stated in the Table 1. During the experiment a solution which is coloured brown was created and the rubber became significantly softer and more absorbent. The final weight of the sample before the reaction was 2.04 g. After about 60 minutes of reaction the weight raised up to 2.24 g.

Fig. 5 rubber sample before attempting a HNO_3 and after 60 minutes, and microscopic images



Proposal of Leakage Disposal

Proposal 1 – Leaks from tank

With the loss of tightness it is important to try to close the leak sealing compound (acid-resistant) and acid then need to be pumped into another tank or vessel. The pump used must be acid-resistant, which is the most

frequently made of plastic (Figure 6). If the damaged tank has the empty chamber (section) the acid can be pumped out of the damaged section in to the blank section, which is standardly left empty from safety reasons.

Figure 6 Pneumatic acid diaphragm pump

Proposal 2 – A crack in the tank

At situations where there is a puncture in the tank its size matters. In case of smaller cracks it is possible to stop the leak the acid devices for sealing cracks (a seal wedge, sealing compound, strap etc.). For larger cracks it leads to leakage of the acid that can be rapidly pumped out of the tank, either intact, and the empty chamber, and a new tank or collection container.

Proposal 3 – Improper tank

When using an inappropriate type of tank, leaking acid is very difficult and often impossible to stop. Tank is broken in several places, and it forms new and new cracks. Pumping of the acid into a new and suitable tank or collection container should be started immediately. Mind the sewage network in surrounding area. The acid resistant pillows need to be used to cover the sewage covers to prevent its contamination.

Nitric acid is most commonly disposed off by neutralization with hydrated lime. A further decontamination agent can be sodium carbonate or

potassium carbonate, or a solution of lime milk. Also improvised materials can be used e.g. a soil, a sand, a crushed limestone or a cement.

Figure 7 Neutralization of nitric acid leak hydrated lime

Attempts fuel with nitric acid were performed by determining the ratio of sample to alkali. They were most common ratios of 1: 1, 5: 1 (5 parts of the sample tank: 1 part HNO_3), and the fuel ratio of 13: 1 (13 parts of oil: 1 part HNO_3).

When you try to gasoline have changed the colour of gasoline and was visible boundary between gasoline and acid. In the experiment with diesel in various proportions to the formation of a precipitate it occurred, respectively. what was more oil, the precipitate was visible. The results of experiments with motor oil creates less dense oil and changed its color to pale. The color change occurred in the reaction and the cooling liquid, where in the substance is changed to light blue.

In these experiments, we expected response turmoil since the safety data sheets (or academic literature) often report an increased possibility

of fire and explosion, combined with the corrosive fuel. From this perspective, the reactions were calm, fully controllable without any indication of an unexpected phenomenon. Most of the samples was the change in the structure visible microscope.

Experiments Material and nitric acid were made by us on various samples of the materials were applied 2 ml HNO_3, and we followed the course of the reaction and the change in the sample materials. Media reaction with the acid was very stormy and expressive, at which there was a leakage of harmful NOx gases and irritating. When the iron experiment initially be run peacefully, after 90 minutes, there was a vigorous reaction and release of harmful NOx gases and irritating. The reaction of aluminium and ABS plastic was peaceful and without visible changes occurred only damage that was visible to the microscope. Last examined samples were rubber (tire) and asphalt. Rubber when exposed to acid softened and turned clear solution was strongly absorbing. Asphalt applications after acid was significantly softer and it was easy to make an indentation into it.

For these experiments show that in terms of safety should be avoided contact corrosive of iron and copper, which are increasingly found in the transport unit and of leaking acid can damage the vehicle. Especially risky is corrosive effect on iron, which from the beginning of the reaction occurs without visible signs, but after about 90 minutes, there is a very strong reaction with visible corrosive to iron.

Another danger is clear from the reaction of nitric acid with rubber (tires), which upon contact with the acid becomes significantly softer and absorbent. Cracking occurs on the surface of rubber material that undermine the integrity of the surface. In contact with the asphalt acid vigorous reaction occurs (boiling acid to the asphalt), wherein the time of the asphalt loses its hardness and caustic spill over into the upper layer (an increase in the porosity of the surface of sample asphalt).

When released caustics from the tank or from another tray (eg. stationary) The immediate requirement is such as to prevent puddles from which under appropriate meteorological conditions (eg. wind, higher air temperature and the earth's surface, higher humidity, etc.). An increase in evaporation acid and its response with the environment (smoky effect – "acid smokes"). In this case, it is appropriate to establish catch hrádzky of inert material to prevent its further fluid to flow along the surface of the ground and establish a sorbate that can be easily removed from the surface than in the liquid.

If the directly affected equipment and gear-cutting or members of their body surface, it is necessary to immediately start by washing (rinsing) water jet, which washed away and diluted alkali. The decontamination process is simple, in practice sufficiently effective and fast, in contrast to time, technical and material-demanding procedure and the subsequent application of a suitable neutralizing agent.

References

1. Čajda A., *Bezpečne s nebezpečnými vecami*, Bratislava 2015.
2. J. Došek, J. Kokeš, *ADR*, Praha 2007.
3. Karta bezpečnostných údajov, Ministerstvo hospodárstva Slovenskej republiky, http://www.economy.gov.sk/kartabezpecnostnych-udajov/142568s (accessed: 11.03.2016).
4. Kemler a UN – označování nebezpečných látek při silniční přepravě. Požáry, http://www.pozary.cz/clanek/50601kemler-a-un-oznacovani-nebezpecnych-latek-pri-silnicni-preprave/(accessed: 11.03.2016).
5. Sbor dobrovolných hasičů Praha – Zličín: Identifikace nebezpečných látek – Kemler kód, http://www.sdhzlicin.cz/index.php?option=com_content&view=article&id=101:id entifikace-nl&catid=51:nebezpene-latky&Itemid=74 (accessed: 11.03.2016).
6. Bezpečnostnílisty,PENTA,http://www.pentachemicals.eu/bezpecnostni-listy.php?subcat=12#seznam (accessed: 11.03.2016).
7. *Ročenka dopravy a telekomunikácií 2013,* Štatistický úrad Slovenskej republiky, http://www7.statistics.sk/wps/wcm/connect/a87b6926-af10–4733–9582-e0765ad2fb6e/Rocenka_dopravy_post_a_telekomunikacii_2013.pdf?MOD=AJPERES&CACHEID=a87b6926-af10–4733–9582-e0765ad2fb6e (accessed: 11.03.2016).

Cite this article as:

M. Orinčák, J. Müllerová, *Specificity of Leaking Nitric Acid From a Tank Vehicle*, "Security Dimensions. International and National Studies", 2017, no 21, p. 62-74, DOI 10.24356/SD/21/3.