

# The Conversion of Liquid Rocket Fuels

Edited by

## Wolfgang P.W. Spyra and Kay Winkelmann

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The Conversion of Liquid Rocket Fuels Risk Assessment, Technology and Treatment Options for the Conversion of Abandoned Liquid Ballistic Missile Propellants (Fuels and Oxidizers) in Azerbaijan

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edited by

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We would like to thank Katherine Fischer for the outstanding and committed help she gave to the production of this publication. Katherine Fischer is a Fulbright Scholar and is conducting research at the department of Chemical Engineering and Hazardous Waste at Brandenburg University of Technology in Cottbus.

We would also like to thank Dr. Ayaz Efendiev for his committed help in organizing this workshop in Baku and for extending his hospitality to all the workshop participants.

Prof. Dr.-Ing. Wolfgang P.W. Spyra

## PREFACE

Prof. Dr.-Ing. Wolfgang Spyra Brandenburg University of Technology in Cottbus, Germany

The demilitarization and conversion of military properties worldwide has been a topic of growing importance since the end of the Cold War. The slowing of the arms race brought on by weapons treaties and relaxed tensions between NATO and Warsaw Pact nations caused stockpiles of conventional weapons to become superfluous. The need to process and dispose of such weapons began more quickly in NATO countries. This demilitarization process began shortly after the reunification of Germany and was largely completed by the mid to late 1990's. The remaining process, no small task in itself, of converting lands formerly used by the military into safe and environmentally acceptable landscapes may continue for decades to come.

Due to a lack of resources and technology, the process of demilitarization in the former Warsaw Pact countries has launched more slowly. In 2002 both Georgia and Moldova finished projects which destroyed their stocks of liquid ballistic missile components. Both these projects were carried out through the cooperative support of trans-national organizations, private contractors, and research institutions.

The Republic of Azerbaijan now finds itself at the beginning of its demilitarization process. Stored at the country's military depots are over 2000 tons of missile fuels, oxidizer, and chemical additives. This hazardous waste is kept in tanks intended only for temporary transport and storage. The tanks are not longer able to contain the toxic liquids and place the environment and human population at acute risk. Furthermore, the destruction of such abandoned missile components is needed as an important part of the demilitarization process. Every litre of destroyed munitions is one less litre to be released as an environmental pollutant or to accidentally fall into rogue hands and be misused.

With a concern for the global safety as well as for the well-being of the Azeri people, a NATO Advanced Research Workshop was

#### NATO Advanced Workshop in Azerbaijan

organized to take place in Baku, Azerbaijan, in November of 2003. The co-directors of the workshop were myself, Dr. Wolfgang Spyra, professor of Chemical Engineering and Hazardous Waste at the Brandenburg Technical University in Cottbus, Germany, and Dr. Ayaz Efendiev, acting chairman of the Department of Chemical Sciences at the Azerbaijan National Academy of Sciences in Baku.

The NATO Partnership for Peace (PfP) has named Azerbaijan as a partner nation, meaning it is eligible to apply for PfP support and funding. This Advanced Research Workshop brought together scholars, scientists, and military personnel from thirteen countries with the goal of examining the practical and technological options available to treat the military waste situation in Azerbaijan. The open forum of presentations and discussion served as a platform for participants from both NATO member nations and partner nations to share their ideas and learn from their colleagues.

Included in the following pages are the background information and treatment options discussed for the situation in Azerbaijan. Also included is an introduction into the NATO Maintenance and Supply Agency's (NAMSA) Partnership for Peace Program, which serves as the lead administrator in the destruction of small arms and light weapons. Finally, an after workshop report prepared by co-director Dr. Wolfgang Spyra will lay forth the results of the workshop and discuss a possible implementation plan.

On the path to a more peaceful geo-political situation, the following text serves as a hopeful example of what trans-national idea sharing and co-operation can achieve. For immerging nations such as Azerbaijan, it is precisely such co-operation that ensures continued academic and technological development.

Brandenburg University of Technology in Cottbus, Germany 3, February 2004

## THE NATO PARTNERSHIP FOR PEACE TRUST FUND: THE PROCESS AND THE ROLE OF THE NATO MAINTENANCE AND SUPPLY AGENCY (NAMSA)

Presented by Steve Brown

Senior Technical Advisor Partnership for Peace Projects Group—Ammunitions Sector NATO Maintenance and Supply Agency

Abstract The NATO Partnership for Peace, PfP, assists PfP nations destroy antipersonnel mines and other light weapons. The Program considers projects on a case-by-case basis. Nations must agree to follow the NATO process of creating a feasibility study, proposing and outlining a means of completing the project, and agreeing on full disclosure of stockpile details during the completion of the project. This paper gives further details of the role of the NATO Maintenance and Supply Agency, which operates as the organising force in demilitarization.

### 1. GENERAL

The NATO Partnership for Peace (PfP) Trust Fund was established in November 2000, as a mechanism to assist PfP nations to destroy antipersonnel mine stockpiles under the Ottawa Treaty. Since then it has been extended to encompass destruction of Small Arms and Light Weapons (SALW) and conventional ammunition and logistic support to defence reform activities.

Projects are considered on a case-by-case, project-based footing. Nations are responsible for developing proposals and presenting them to a special meeting of the PMSC in EAPC/PfP format. A proposal must be sponsored by at least one NATO member and one Partner nation, normally the host nation, with

overall responsibility for the development of the proposal, for securing project funding and reporting on project progress.

## 2. AGREEMENTS

In order for NAMSA to undertake this work, a number of Agreements will need to be prepared these include:

- Memorandum of Understanding (MoU) between the Partner Country and NAMSA which is the umbrella agreement enabling NAMSA to work in the country.
- An Implementing Agreement between the Partner Country and NAMSA as an annex to the MoU specifying the obligations of each in implementing the project.
- Executing Agent Agreement between the Lead Nation and NAMSA specifying the obligations of each in implementing the project.
- Financial Management Agreement between the Lead Nation, NATO Financial Controller and donors to formalise pledges sufficient to implement the project. NAMSA is only able to enter into commitments when sufficient funds had been committed by donor nations.

## 3. FEASIBILITY STUDY

## 3.1 Letter of Intent

NAMSA is tasked by a Letter of Intent (LOI) to undertake the Feasibility Study and produce a proposal detailing budgetary costs methodology and timeframe for approval by the Trust Fund. The LOI will specify the requirement to be addressed and will include the fee to be paid to NAMSA to cover travel, subsistence and personnel costs.

## 3.2 Elements of Feasibility Study

The Feasibility Study will examine all relevant technical data, undertake visits and detailed technical discussions aimed at assessing the full extent of the task, the requirements to address the task, the capability of the host nation, the shortfall in that capability, the options to overcome any shortfall including enhancing the capability or using third party facilities. It will include the following:

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- Full technical information relating to the ammunition and weapons stockpile, including site visits where appropriate.
- Assessment of the demilitarization requirement, options and potential disposal methodologies appropriate to the stockpile including discussions with industry where applicable.
- Assessment of existing in-country demilitarization capacity and identification of future additional demilitarization resources against the requirement.
- Identification of potential in-country and external sources for demilitarization and other equipment, logistic support, specialist skills, training capacity etc with costs.
- Consider the effect of relevant policy, operational and other activity on the project.

## 4. **PROJECT PROPOSAL**

The Feasibility Study will result in the preparation of a full technical proposal detailing options considered, recommended solution, timeframe for implementation, accurate budgetary costs, possible suppliers etc. The contents of the proposal are summarised below.

## 4.1 Outline Concept

The proposal will include a statement of the overall concept for the project, identifying specific technical and operational aims, assumptions and, where appropriate, any options that were considered and accepted or rejected. It will also include a timeframe for the project broken down into phases.

## 4.2 Stockpile Details

The proposal will summarise details of the stockpile in terms of quantities, types, condition, location and other relevant information. It will also include if applicable any riders concerning the veracity of the information and plans for future subsequent verification. It may also provide technical information to illustrate the stockpile.

## 4.3 Demilitarization Methods

NAMSA favours environmentally benign demilitarization methods which normally precludes expedient solutions such as open detonation. The proposal will identify the methods and equipment to be utilised in support of the project. The usual aim will be to source the majority of equipment and

tools in-country to minimise costs and to maximise the socio-economic benefit to the country. Where these are not available, such as in the supply and installation of major demilitarization equipment these will be purchased internationally under NAMSA's normal rules of competition, unless a contributing nation or agency offers to supply the equipment as its contribution to the project. The proposal will identify details of the methodologies to be employed, key equipments and outline technical specifications.

## 4.4 Demilitarization Facilities

The proposal will identify and assess any existing in-country demilitarization facilities with recommendations for enhancements to infrastructure, facilities and training to overcome any identify skill gaps.

## 4.5 Logistics

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The proposal will identify the logistic support required for the project, and incountry or, where appropriate, external sources of supply for that support. Logistics could include security provision, selection, inspection, repacking and loading /unloading of weapons and ammunition, transportation, storage and provision of office facilities.

## 4.6 Acquisition Plan

The proposal will provide an outline of the acquisition plan for equipment and services in line with the proposed timeframe of the project. The plan will specify how and when NAMSA will issue Requests for Proposal (RFP) for the supply, installation and commissioning of equipment and provision of services. These RFP will include technical requirements, statements of work, timeframes for delivery and other contractual requirements.

## 4.7 Project Management

The proposal will identify the general management structure for the project including the NAMSA Luxembourg-based support and its in-country project supervision, verification and auditing team. This will identify the mix of international and national staff making up the team and provide job descriptions for the key posts.

## 4.7 Financial Estimate

The proposal will include a detailed budgetary cost estimate for the project. It will include a breakdown of the calculations and assumptions on which the budget was arrived at and will include the cost of key equipments, services and other capital expenditure, salaries, operational costs, insurances, travel, administrative costs including NAMSA charges and any contingency.

## 4.8 Media Plan

Guidelines for the Trust Fund require that a Media Plan should be submitted as part of the project proposal, this will be provided in outline and identify any specific media events or activities, including the use of specialist advisors, where appropriate.

## 5. **PROJECT IMPLEMENTATION**

Once the proposal is accepted and agreements are finalised NAMSA can undertake full implementation as Executing Agent. This will involve Project Management and real time supervision, issuing and assessing requests for bids to contractors, letting and managing contracts and sub-contracts, authorizing payments, verification and auditing of contractors, producing reports to NATO HQ and Lead Nation. The main activities are summarised below.

### 5.1 Personnel Recruitment

NAMSA will normally employ its Project Management team on consultant contracts, negotiated and administered by NAMSA's Procurement and Personnel Divisions, following a formal recruitment process from a list of candidates both for international and national personnel. Consultant contracts will cover fees, travel expenses, reimbursement for incidental expenditure, working hours and entitlement to leave. Personnel will also normally attend a short training period at NAMSA, Luxembourg for familiarization in NAMSA procedures as well as pre-project briefing.

## 5.2 Contracting

All contracts to undertake tasks, services or provide equipment will be done through the normal formal NAMSA contract procedure. This will include:

#### 5.2.1 Request for Proposal

Formal Request for Proposals (RFP) including detailed Statements of Work are produced for all activities. The Statement of Work will normally detail required outputs and specified technical, environmental and other limitations but will not specify how the contractor should do the work. The RFP is issued to selected sources identified through the NAMSA Source File system.

#### 5.2.2 Bidder's Conference

For technically complex or high risk activity a Bidder's Conference may be convened. This will normally take place in-country and at the operational site. In certain instances attendance is deemed compulsory and bids will only be accepted from sources that are represented at the conference.

#### 5.2.3 Award of Contract

On receipt of bids the normal NAMSA contractual award process is applied to select the contractor. This involves scrutiny of the technical content of the bids and responses to any supplementary questions from NAMSA to confirm which, if any bids are technically compliant. It is only after that compliance is assured that the price offered by the contractor is considered. The compliant contractor who offers the lowest price is normally awarded the contract.

#### 5.2.4 Importation of Equipment

NAMSA and its local representative will assist in securing the necessary export and import documentation from the in-country authorities. Much equipment used in demilitarization may be classed as dual purpose and require special authorisation to both import into the project country and export from the home country.

#### 5.2.5 Training

Where training is necessary as part of the capacity building part of a project, such as for host nation military or technical personnel, NAMSA can identify the type of training necessary, identify sources to provide the training and contract the source to undertake the training. NAMSA will visit the training establishment to ensure that the training is as required.

#### 5.2.6 **Operational Phase**

NAMSA will be present to assist, advise and supervise all stages of the operation from the move onto site, commissioning, training, completion and demobilisation. This will ensure that operations are undertaken safely, adequately, on time and in line with contractual requirements.

## 5.3 Project Management

These projects are managed by the PfP Projects Group of the Ammunition Section under direction of the Program Manager of NAMSA's Special Projects Program. NAMSA's supporting divisions responsible for finance and contracting provide additional support. Specific management tools employed to support these projects include:

#### 5.3.1 **Project Plan and Milestones**

The guide for managing the project, including the milestones and detailed budget, is provided by the project proposal. Approval for any significant deviations are sought from the lead nation.

#### 5.3.2 Coordination of Effort

Regular project management meetings and a system of written reporting ensure the distribution of information at all levels. These include:

- Weekly coordination meetings held by the Program Manager of the Special Projects Program which are attended by project management, finance and contracting personnel.
- A weekly situation report is sent to the Director of Logistics Programs and Operations, who distributes it to the General Manager and the other Directors.
- NAMSA's project management staff maintain close contact with the in-country supervisory team who submit regular written reports.
- A NAMSA Representative will verify and certify all contractor invoices before forwarding them to NAMSA.
- NAMSA provides written quarterly reports to the Lead Nation, which are also copied to the International Staff at NATO Headquarters. On the completion of the project a comprehensive Final report is written that will highlight the achievements, progress and lessons learnt from the project.

• NAMSA Luxembourg staff undertake regular in-country project management visits to observe and monitor the project and discuss relevant matters with in-country authorities.

#### 5.3.3 Contract Management

PfP Projects Group prepare Statements of Work for all contracts including those for internationally and locally employed personnel, operational activities, transportation and other services and tasks. These are passed to the Special Projects Program's specialist contracting personnel for contracts to be prepared, negotiated and issued.

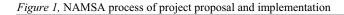
#### 5.3.4 Financial Management

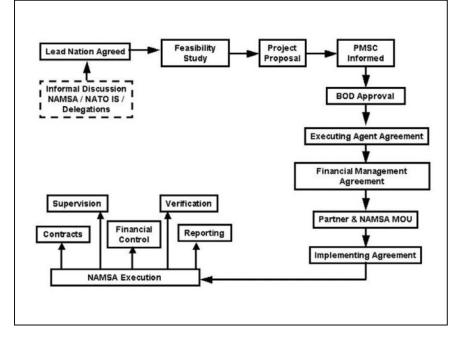
NAMSA considers it essential that projects are managed to a successful conclusion within budget. Given the limited time and resources available for developing PfP Trust Fund proposals and the difficulty of budgeting for what are often innovative processes, it is essential to retain a certain degree of flexibility. Budgetary control is a continuous process, which is reviewed against a weekly financial statement prepared by the program's finance staff. A financial statement was also included with the project reports sent every 3 months to the Lead Nation. Routine financial work of processing and paying invoices against the various contracts is conducted in accordance with NAMSA's normal procedures.

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#### 6. SUMMARY OF THE PROCESS

A summarised visual of the NAMSA process can be seen in Figure 1, below.





## THE EVOLUTION OF RISK IN THE 1990'S

#### Prof. Dr.-Ing. Wolfgang Spyra

Brandenburg University of Technology in Cottbus, Germany

- Abstract This is an introduction into the theme of military base conversion and demilitarization. The background of the Cold War shows how the risks have changed over the past few decades. This artile helps to understand the situation that Azerbaijan now faces with a surplus of operational and deployment resources.
- Keywords: Cold War, NATO, Warsaw Pact, Soviet Republics, demilitarization in Germany, restructuring, social aspects of conversion, demilitarization, challenges to conversion, means of conversion, funding conversion.

## **1. INTRODUCTION**

After the end of the second world war the victorious Allied Forces who had joined together to defeat Germany, disbanded and formed two powerful blocks. On one side was the Eastern Block, ruled over by the Soviet Union, and on the other side were France, Great Britain and the United States, who together formed the elements of the Western Block.

As East and West powers built political and economic alliances, the impact of this new polarized political climate spread to lands outside of Germany. The military sectors of the West formed the North Atlantic Treaty Organization (NATO). To counter-act NATO, the Soviet Union established the Warsaw Pact. The line of separation dividing the east and west powers formed the so called "Iron Curtain," the symbol of the decades long Cold War between the eastern and western blocks.

A trend in the late 1980's and early 1990's towards political harmonization between the two blocks eventually lead to the collapse of the powerful bilateral structure. What was left of the Soviet Union was a large, centralized Russia, which held varying degrees of diplomatic relations with the other

former Soviet states. Diplomatic relationships ranged from cases of mutual, political, and economic cooperation, to situations where former block politics were completely rejected. Political changes after the fall of the Soviet Union led domestic policies to focus on new pressing issues, most obviously acknowledging major economic instabilities.

## 2. DISMANTLING MILITARY POTENTIAL

As a consequence of economic hardships, political and economic structures of the former Soviet Republics were forced to undergo major changes. A priority was placed on budget analysis within the various governmental sectors, such as the military. Military sectors in both blocks found themselves confronted with major budget cuts. Once the Cold War ended and the level of threat and danger diminished, maintaining the massive defence departments of the past few decades was no longer justifiable. The need for large-scale military base conversion was thus born.

In those nations where the military played an extremely powerful role, relative to other governmental agencies, the process of conversion brought considerable problems. This can be understood, seeing that the conversion process in many countries was made possible only through the help of foreign aid, and this foreign aid often came from countries the civilian society historically understood only as the adversary.

Conversion means the dismantling of military potential, which includes:

- Significantly decreasing the magnitude of combat forces
- Reducing management and operational resources
- The transfer of occupied lands back to the public for civilian use.

In terms of sustainable steps toward world peace stability, conversion a positive sign. In terms of domestic peace and social tolerance of political restructuring, however, conversion measures present a considerable burden which contains a potentially "explosive" social element.

### 3. THE BURDON OF RESTRUCTURING

For the dismantling and rebuilding of a country to be successful specialists are needed. Soldiers are specialists. During the Cold War around 80% of all scientists in Russia were employed by the military. When such specialists are released from military duty, they find themselves in a labour market that

demands neither their qualifications nor the sheer mass of labourers they present. With few exceptions, this is a global phenomenon. Since 1992, over 1.2 million military personnel have become unemployed through restructuring. As unemployment rates raise and people are unable to provide for the basics of life, this leads, inevitably, to social stress, if not to all out domestic conflict. Therefore, military conversion applies not only to land parcel and facilities conversion, but also to a social conversion. Indeed, conversion also involves a change in conceptual thinking. New conceptual thinking leads to societal restructuring.

## 4. NECESSARY STAGES OF CONVERSION

Shrinking military potential includes, as a general rule, the disposal of military equipment and the suspension of management and organizational resources. In Russia, disarmament meant dealing with а gross overcapacitation of armaments. In Murmansk alone, 52 submarines with nuclear capabilities sat in the harbour, out of commission. Globally, the possibilities of reselling decommissioned military equipment is practically null. Only certain special land crafts or vehicles which can be marketed inexpensively are available on the world market. Tanks and many other land crafts must simply be placed out of operation. The funding to undergo other reuse options is simply not available. Surplus operational resources are simply gathered into concentrated locations and are appraised for possible future use as scrap material.

Because of the economic and labour structures organized by the former Soviet republics, the scrapping of machinery itself can also be problematic. In theory, only consumer goods for the specific country should be produced from the scrapped military equipment. In practice, however, often times new military machinery has been produced. Here, it is important to take note that the development of advanced technologies was emphasized and established only in Russia. It must follow, then, that reusing materials in an economically viable way is only possible in certain locations. In the cases of most former Soviet republics, extremely long export distances in and out of Russia are no longer affordable. The priorities or financial resources are elsewhere. As a result, military equipment is gathered into these well-known machinery cemeteries.

The same problems are shared by not only the Army and its surplus of tanks, but also for the Air Force and its fleet of jets which may or may not be able to

fly, and also for the Marines whose fleets would out-run an enemy only occasionally.

Not discussed here are two additional factors: the source of funding of conversion, and problems resulting in acute danger to human health and safety. Indeed, it is clear, that the world community appraises these dangers in highly variable ways.

One possible way for the military to cut costs is by giving-up some, or most, of its occupied land. The declining number of enlisted troops makes the transfer of barrack use increasingly more possible. Likewise, giving training grounds back to the cities or communities appears to be the easiest solution in the context of the problems already described. National politics plays an important role in determining how the military can act. After all, politics is what controls the amount of funding allocated to future projects. Military management, as a general rule, is bound with the responsibility to communicate with the political sector about possible consequences political provisions may have on national defence and to take-on the total responsibility for these consequences.

## 5. CHALLENGES OF CONVERSION

The problems of conversion are more complex and diverse than one may originally think. Conversion in the area of military and armaments residual wastes means, in general, the transition from a military use to a civilian use. Once combat forces have been reduced, it follows that military units also give-up their bases. It is important that opinions and input from civilian groups be a part of this process. After all, it is in the daily lives of the local communities that the repercussions of military settlement were most strongly felt. Around each military base an economic life developed, which was lived and supported primarily by the soldiers. With the withdrawal of the troops a significant economic factor was lost. In some areas the military personnel had been the only economic factor in the region. The unbalanced structure left behind were not brought to balance by political actions, rather as a general rule, they have had to be newly established through a process of resettlement. This theme is as multi-faceted as it is difficult and, as with the theme of conversion, calls for the work of professionals.

The basics of conversion are to design and to remove the military potential and from the military instillations. Facilities such as barracks, warehouses, repair stations, social service areas, training grounds etc. are the existing facilities that need to be dealt with. The military capital which is able to be mobilized will be transferred to existing facilities, thus concentrating the storage of weaponry, fuels, or other military excess into fewer locations. Often the dangers resulting from the transportation and storage of military goods are underrated by the general public.

Although it appears that high levels of exposure could effect the civilian population without them knowing it, for citizens threatened by unknown dangers the only acceptable choice is to live up to the demands imposed upon them to protect their safety.

## 6. PRACTICAL EXAMPLES OF DANGERS IN CONVERSION AND TRANSFERRING RESOURCES

It has been established that with the evacuation of military lands, the management and operational resources have been transferred to other military locations. The locations to which these resources have been transferred stand out as being especially safe against an outside attack. Indeed, it is important to assure that these management and operational resources do not fall into unauthorized hands and misused. Experience shows that in many cases the transfer of equipment from one location to another occurs without incurring additional dangers.

In some cases, munitions and combat materials are transported to other military installations for storage, at which locations munitions or hazardous facilities are already present. In other cases, military materials are transported and stored in areas outside of the military realm. In these cases the level of security may be called into question. Hence depending on the conditions of transportation and storage, dangers can either be compounded or negated. In the cases we are aware of, the only disadvantage we encounter is in the case of an emergency, where only experts with a specialization in dealing with this specific type of danger would be able to combat a dangerous situation. This means that a dangerous situation or an accident would not be able to be handled adequately.

Further practical examples shows that often munitions which were planned to be moved to a new location were prepared for transportation, but never moved. There are further cases where although the munitions actually were transported to a new location, the trains with over 100 freight cars full of munitions were never unloaded. Security and surveillance is also often lacking. In some cases, it may be possible for persons lacking technical

knowledge or permission to gain access to the hazardous substances. An instance of misuse is, therefore, not unimaginable and builds the potential for terrorist activities.

#### 7. THE ROLE OF PERCEPTION IN CONVERSION

Measured in terms of civil standards and given the possibilities of the United Nations, the World Bank, NATO, NGO's etc., it is impossible to understand the grossly negligent way in which decommissioned munitions are being handled.

Above all, there is still a grey area. This grey area is seen in the way the military carries out the evacuations of its installations. On the one hand, the defence sector expects the civilian population to contribute technical knowledge to the process, but such technical knowledge is not readily available. On the other hand, the military themselves have mishandled information concerning the quality of the evacuated sites, misinterpreting the information and reaching false conclusions.

What distinguishes soldiers from other professions is their possession of specialized knowledge unique only to those who have had military experience. Even basic information on handling weapons and munitions is largely unknown by civilians. The type of "forgotten" residual waste at the sites depends on the way each individual site was used, for instance if it was a firing range, a training grounds, or a munitions demolition area. This factor is undesirable.

Nevertheless, it is the civilians who are in the most serious danger of coming in contact with these hazardous materials. In many nations the land owner is liable for dangers existing on his or her land. Therefore, when a parcel of land is taken over from the military in good faith, and an assurance is given that the land will be left in clean and sanitary conditions, one must rightly ask the question, "how clean is clean?" And still, this question does not address issues of liability for damages to human health and safety. The reason for this may be that in many countries military lands are given-up, but not with the intention that they will be used by the general public.

Another important issue deals with differences in the interpretations of shared concepts. A useful example to illustrate this point is the withdrawal of Soviet combat forces from Germany. The withdrawal of Soviet troops was carried-out in a well planned and organised manner. The Russians had agreed with

German officials that the lands would be left clean. In this case "clean" was meant in a German legal sense. German and Russian officials cooperated to allow household waste, industrial waste, and other wastes from the Russian troops to be received and processed by German service facilities. This cooperation was one way to successfully lighten the work load of future land owners. The military facilities and land installations were left in sanitary conditions. Some areas were even found swept clean. Indeed, the age old practices of cleanliness, so well loved by the Germans, had been taken seriously by the Russians over the past few decades. Nevertheless, the Russians had buried garbage which should have been processed and properly disposed of and this lead to hazardous waste situation.

The Russian officers in charge of preparing and cleaning the facilities for evacuation where instructed to leave the area in sanitary conditions; however, none of the soldiers were aware of what "sanitary" meant in the sense of German legality. The Russian side had interpreted "clean" as it had always been interpreted in the military sense. Both sides were correct.

In this examination we have still not mentioned those problems which demand workshops such as this one, where we will seek solutions in the disposal of liquid rocket propellants and the destruction of chemical war agents. To preserve the safety of the common good, defence sectors have secured combat materials and munitions which are no longer needed in operation. However, these materials pose a threat to human health and safety if the correct actions are not taken to store them properly and responsibly. Through this workshop we will learn the importance of supporting such responsible actions.

## WEAPON SYSTEMS USING SAMINE, MELANJ AND ISOPROPYL NITRATE

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- Abstract This paper describes the uses and properties of three chemicals stored in Azerbaijan: melanj, samine, and isopropyl nitrate. These three chemicals have historically been used in the manufacturing of liquid ballistic missiles. Also included in this report is a description of how the liquid complements and mechanics of the rocket function to launch the missile.
- Keywords: Weapons systems; application of rocket engines; operation of bi-component liquid rocket engines; properties of melanj; samine, isopropyl nitrate; rocket engines S-200 S-75, 8K-14; combustion chamber; auxiliary systems.

### 1. INTRODUCTION

Components of rocket fuel such as samine, melanj, and isopropyl nitrate are used in the liquid rocket engine (LRE) developed in the end of the 1950's and 1960's.

These liquid rocket engines are used in many rockets both in tactical types 8K-14 and in antiaircraft rocket complexes of S-200, S-75 types.

The application of liquid rocket engines has enabled the defense industry to provide rocket flights of uniform speed on all flight trajectories, which has essentially facilitated the management of the rocket during flight and assured its optimal speeds at all altitudes by application of adjustable thrust. This has, in turn, enabled an increase in the rocket's range of flight.

Usually, liquid rocket engines are used to create thrusts necessary for the rocket's second stage of flight and represent the single-chamber liquid rocket engine with a turbo pump system of fuel supply. It operates with a bicomponent auto-igniting fuel consisting of two components: samine and

melanj. The engine aggregates supply the oxidizer and fuel simultaneously to the onboard source of power (OSP).

## 2. ROCKET ENGINE OPERATION

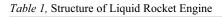
Liquid rocket engines consists of three main units and three auxiliary systems (see Table 1).

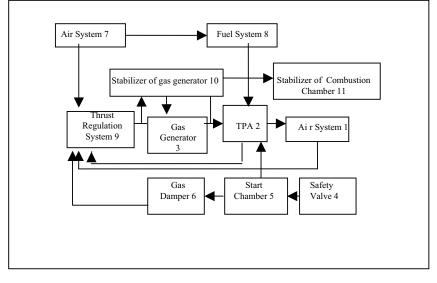
#### Main units

- Combustion chamber
- Turbo pump aggregate (TPA): 2
- Gas generator: 3

#### Auxiliary systems

- System of start: 4, 5, 6, 7, 8:
- Thrust regulation system: 9
- Stabilization systems of two components: 10, 11





Thus the bi-component liquid rocket engine functions in this way: the combustion chamber creates the necessary fuel pressure for an input into the turbo pump aggregate (TPA) and gas generator. The main units of the TPA are the turbine, the oxidizer pump and the fuel pump. The gas generator builds

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gas pressure and transfers the pressure to the bi-component chamber of combustion in which the same components as in the LRE are moved.

The system of start services the start-up of the mid-flight engine. The system of start varies in different engines and can either be autonomous or forced.

The main advantage of an LRE is its ability to program engine thrust regulation that allows the rocket to reach optimal speeds.

The disadvantages are its operational complexity in relation to the aggressive poisonous liquid components used in its operation. These liquid components endanger operational personnel.

The work of implement installation can be divided into several stages. The main stages of operation are pre-launch preparation, start mode, and flight mode.

The program installation is made at the pre-launch preparation mode, thus the control stress is moved to the engine from the ground equipment, therefore there is an installation of beginning of LRE work of given program.

The operation at start mode begins by the pressing the "START" button. At the enactment of the "START" command +27B is moved to the pyrotechnic valve of the air start system. After that, the air from the sphere-cylinder acts as a gas shutter and the outside source of power, OSP, besides these by this command the program installation from locating equipment is ceased.

After output into the OSP and transition on the outside source of power, +27B of pyrocartridges from the start engines are released, thus the gases from the chamber of combustion from the upper start booster are moved to the gas shutter, the membrane units, and the safety valve of the start chamber. Thus, there is an opening of the gas shutter, break of membrane units and opening of safety valve.

As a result, the air from the sphere-cylinder goes to the fuel tanks through a gas shutter, through a reduction gearbox and membrane units.

The operation of implement installation at flight begins at the moment the rocket separates from the start installation. Once it achieves high-speed, the head of the value reaches  $0,65 \text{ kgs/cm}^2$  and the pressure warning indicator calculates and submits the stress on the pyrocartridge of the start chamber. Thus the grains ignite in the start chamber and form gases go to through the

turbine of the TPA and start oxidizer and fuel valves which are opened and open access to components in the TPA pumps.

The turbine acts as a pump to move pressurized fuel into the combustion chamber, into the gas generator, and into the OSP. Thus the LRE is started, and the gas generator and OSP pass to power of their tanks.

Upon reaching fuel pressure in the cooling chamber  $(15 \text{ kgs/cm}^2)$  the pressure warning indicator gives out the stress on the executive engine EMTR (executive mechanism of thrust regulation) and from this moment the thrust regulation begins.

After the start engines have finished their function they separate from the second stage of the rocket.

From this point forward the implement installation works with the given program. The engine will cease operation when fuel component supplies have been exhausted.

#### **3. PROPERTIES OF COMPONENTS**

In 8K-14 rockets, the oxidizer AK-2761 is used (Table 2), while on S-200 a AK-27P oxidizer is used and on S-75, the oxidizer is AK-20K.

Table 2, Properties of AK-2761

Nitric acid	HNO <sub>3</sub>	70%;
Nitrogen Oxides	$N_2O_4$	24-28%;
Inhibitor of corrosion		0,2%.

The oxidizer AK-27P presents a volatile, highly toxic and aggressive liquid which is orange-brown in color with the following properties (Table 3).

Table 3, Properties of oxidizer AK-27P

Nitric acid	at least 69,5%
Nitrogen Oxides (in recalculation of N2O4)	24-28%
Water	0,7-1,7%
Fluoric hydrogen	0,3-0,55%
Orthophosphoric acid	0,05-0,15%
Mechanical impurity,	at least 0,02%
Density at 20 <sup>o</sup> C	$1,592-1,616 \text{ g/cm}^3$
Boiling Pt. (depending water and nitrogen oxides)	+(44,6-49,5) <sup>o</sup> C.
Freezing Pt. (depending on water and nitrogen oxides)	– (55,4-61) <sup>o</sup> C.

The oxidizer AK-20K presents the solution of nitric theatracid  $N_2O_4$  in nitric acid. The properties of AK-20K is found in Table 4.

Nitric acid HNO <sub>3</sub> , at least	73,4%;
Nitrogen Oxides (in recalculation of N2O4)	17,5-22,5%;
Phosphoric acid H <sub>3</sub> PO <sub>4</sub>	1,0-1,25%;
Water	1,2-2,8%;
Fluoric acid	0,5%;
Firm rest, at least	0,3%;
Densities at 20 <sup>o</sup> C	$1,575 \text{ g/cm}^3$
Freezing Point	-6172 <sup>o</sup> C;
Boiling Point	+49,5 - +54C.

Table 4, The properties of oxidizer AK-20K

Finally, the fuel TG-02 (samine) presents the mixture of xylidine and triethylamine. Its properties can be found in Table 5.

Table 5, The properties of fuel TG-02

Isomeric oxalis	50%	
Diethylamine and triethylamine		
(Diethylamine at least1,6%)	50%	
Water	at least 0,5%	
Mechanical additives,	at least 01%	
Densities at 20 <sup>o</sup> C	$0,845 \text{ g/cm}^3$	
Temperature of total freezing	-89°C -103°C.	
The fuel TG-02 is an oily liquid of from yellow to dark-brown color with		
characteristic smell.		

## CHEMICAL COMPOSITION OF ROCKET FUEL COMPONENTS: MELANJ, SAMINE AND ISONITE

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Abstract The rocket fuel components melanj, samine, and isonite (isopropyl nitrate) are stored in various places in the Republic of Azerbaijan. The amounts stored in two military depots at Alyat and Mingechevir may amount to nearly 2 million kilograms. Melanj is a nitric acid based chemical, samine is a mixture of xylidine and triethlyamine, and the additive isonite is a product of alcohol and nitric acid.

## 1. PRESENCE OF ROCKET COMPONENTS IN AZERBAIJAN

In various places on the territory of CIS countries (including Azerbaijan Republic) are stored large volumes of rock fuel components are stored, which remain from the times of the Soviet Union. This waste is made up, in particular, by the oxidizer melanj, the fuel TG-02 (samine) and the mono-component fuel OT-155 (isopropyl nitrate).

Said rocket fuel components are stored in central warehouses, fuel stores of the Ministry of Defense and also in some antiaircraft military units in different parts of the Republic of Azerbaijan, in particular near settlements Alyat and Mingechaur. The volumes of said components of rocket fuel are displayed in Table 1.

Oxidizers	
AK-20k	720 922 kg
AK-27p	652 842 kg
AK-27i	104 644 kg
Total:	1 478 418 kg
Fuel	
TG-02 (Samine)	449 482 kg
OT-155 (isopropyl nitrate)	24 489 kg
Total:	473 971 kg
	-

Table 1, Amounts of Stored Rocket Components in Azerbaijan

Of major concern today is the fact that the warranty period of said rocket fuel components has expired. During the inspection trip to the storage sites of these components in October 2003, leaks of rocket fuel components were revealed due to defects in the storage tanks. Such a situation can result in mass poisoning of people (lethal cases or, in some situations, complete disabilities and chronic diseases) and pollution of the environment.

To solve this problem, prior to disposal of rocket fuel components, their chemical composition should be studied for identification of the most environmentally sound and optimum technology of destruction.

#### 2. NITRIC ACID-BASED OXIDIZERS (MELANJ)

Mass fraction of HNO <sub>3</sub>	not less than 89,3-90 %
Mass fraction of H <sub>2</sub> SO <sub>4</sub>	not less than 7,5 %
Mass fraction of NOx	not more than 0,3 %

Oxidizers with a nitric acid base consist of concentrated nitric acid, nitrogen tetroxide, water and anticorrosion inhibitors added for protection of rocket engine equipment and storage tanks. They destroy most non-metallic materials: timber, resin, many plastic materials, textile, cardboard, etc.

Oxidizers with a nitric acid base are hygroscopic; they are characterized by strong oxidizing action and contain 65% of reactive oxygen. They are strong poisons. Due to relatively low boiling point of nitrogen tetroxide (22°C) these oxidizers are highly volatile.

## 2.1 Nitric Acid

Pure nitric acid (HNO<sub>3</sub>) is colorless liquid with density  $1,51 \text{ g/cm}^3$  at  $-42^{\circ}$ C congealing into transparent crystalline mass. In the open air it "smokes", like concentrated hydrochloric acid, as its vapors form small droplets of mist with the moisture contained in the ambient air. Nitric acid is not stable; it gradually decomposes in the daylight.

 $4HNO_3 = 4NO_2 \uparrow +O_2 \uparrow +2H_2O$ 

Decomposition is quicker at a higher temperature and concentration. Released nitrogen dioxide is dissolved in the acid giving it brownish color. Nitric acid is one of the strongest acids; in diluted solutions it decomposes completely into the ions  $H^+$  and NO3<sup>-</sup>.

## 2.2 Oxidizing Properties of Nitric Acid

Oxidizing capacity is characteristic for nitric acid. Many non-metals are easily oxidized by nitric acid, oxidizing into the respective acids. Sulfur, upon reaction with nitric acid is gradually oxidized into sulfuric acid and phosphorus, likewise, into phosphoric acid. Smoldering cinders immersed into concentrated HNO<sub>3</sub> begin burning brightly. Nitric acid acts on almost all metals (except gold, platinum, tantalum, rhodium, iridium) converting them into nitrates, and some metals – into oxides. Concentrated HNO<sub>3</sub> stabilizes some metals. It was known long ago that iron, which is easily dissolved in diluted nitric acid, is not dissolved in cold concentrated nitric acid. Later it was established that nitric acid has a similar effect on chromium and aluminum. Under the effect of concentrated nitric acid these metals are transformed into a passive state.

The higher concentration of  $HNO_3$ , the less degree of its reduction.  $NO_2$  most often releases in reactions with concentrated acid. In reactions of diluted nitric acid with low active metals, e.g. copper, NO is released.  $N_2O$  is formed in the case of more active metals such as iron and zinc. Highly diluted nitric acid interacts with active metals – zinc, magnesium, aluminum with formation of ammonium ion, which forms ammonium nitrate as a result of reaction with acid. Usually several products are formed simultaneously.

Nitric acid acts on many organic substances so that one or several hydrogen atoms in the molecules of organic compounds are substituted with nitrogroups NO<sub>2</sub>. This process is called nitration and is very important in organic

chemistry. Nitric acid is one of the most important compounds of nitrogen. It is widely used in production of nitrogenous fertilizers, explosives and organic dyes and as an oxidizer in many chemical processes. It is also used in production of sulfuric acid (nitrose method) and in production of cellulose varnishes and (cinema) films.

## 2.3 Nitrates

Salts of nitric acid are called nitrates. They are easily dissolved in water, and on heating are decomposed with release of oxygen. Nitrates of most active metals are transformed into nitrites:

$$2KNO_3 = 2KNO_2 + O_2 \uparrow$$

Nitrates of most remaining metals on heating decompose into metal oxide, oxygen and nitrogen dioxide. E.g.

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 \uparrow + O_2 \uparrow$$

Finally, nitrates of less active metals (e.g. silver, gold) on heating decompose into free metal:

$$2AgNO_3 = 2Ag + 2NO_2 \uparrow + O_2 \uparrow$$

Easily detaching oxygen, nitrates at high temperature are strong oxidizers. Alternatively, their aqueous solutions practically do not exhibit oxidizing properties. Nitrates of sodium, potassium, ammonium and calcium are most important.

Sodium nitrate NaNO<sub>3</sub>, or caliche, is found naturally occurring only in Chile. Potassium nitrate KNO<sub>3</sub> also can be found in nature in small quantities, however mainly it is produced by interaction of sodium nitrate with potassium chloride.

Both these salts are used as fertilizers, and potassium nitrate contains two elements required for plants – nitrogen and potassium. Sodium and potassium nitrates are also used in glass manufacturing and in food industry as conserving agents.

Calcium nitrate Ca  $(NO_3)_2$  is produced in large quantities by neutralizing nitric acid with lime; This can be used as fertilizer.

## 3. FUEL TG-02 (SAMINE)

Fuel TG-02 is a mixture of technical isomeric xylidines  $C_6H_4CH_3NH_2$  and technical triethylamine  $(C_2H_5)_3N$ . It is a mobile oily liquid with color from yellow to dark-brown and an odor typical for saturated amines. Mean relative molecular mass is 111,0 (units?). It is used as a fuel component for liquid rocket engines.

Fuel TG-02 self-ignites easily on a contact with oxidizers on the basis of nitric acid, with very short periods of delay of spontaneous ignition.

Fuel TG-02 mixes with many organic solvents: ethyl alcohol, acetone, kerosene, petroleum and carbon tetrachloride. Water solubility of fuel TG-02 is restricted. At 18-23°C mass fraction of dissolved amines is 3,3-3,9%. Share of triethylamine and diethylamine in this percentage is 2,7-3,1%, and that of isomeric xylidines – is 0,6-0,8%. At 18-23°C, 9,3-10% of water is dissolved in fuel TG-02.

Fuel TG-02 is hygroscopic. When stored at  $20^{\circ}$ C in sealed bottles with 100% humidity mass fraction of water, the fuel may reach ultimate values (9,3-10%). This confirms that the fuel should be kept in sealed conditions.

Fuel TG-02 possesses base characteristics. Triethylamine is a strong base, xylidine is a weak base (see Table 2).

№	Feature	Norm
1	Density at 20 <sup>o</sup> C, gram per sm <sup>3</sup>	0,835- 0,855
2	Mass part of triethylamine (total, together with diethylamine), %	49,5-52,0
3	Mass part of isomer xilidines, %	48,0-50,5
4	Mass part of water, % no more	0,20
5	Mass part of mechanical admixtures, %, no more	0,003

Table 2, Technical requirements for TG-02 fuel

Fuel components form salts on interaction with salts and easily hydrolyzed in water.

Fuel TG-02 is oxidized with oxygen from the ambient air very slowly. Light, elevated temperature, moisture and presence of copper ions are catalysts of the process. In real storage conditions where protective seals fail, the quality of fuel deteriorates due to oxidation and flooding.

Fuel TG-02 is not corrosive with regard to iron, aluminum and their alloys. Iron, aluminum and their alloys do not have negative effect on fuel or its long-term storing. Alloys on the basis of iron and aluminum are recommended for use in contact with TG-02. Minor presence of copper (less than 10 mg/l) in the fuel has catalytic effect on fuel, promoting the processes of its oxidation with the ambient oxygen. Hence, it is not recommended to use copper and its alloys for fabrication of facilities intended for operation with fuel TG-02. Non-metal materials most resistant towards TG-02 are fluoroplastics, polyethylene and polyamides.

# 4. MONOCOMPONENT FUEL OT-155 (ISOPROPYL NITRATE)

Isopropyl nitrate is the product of etherification of isopropyl alcohol of nitric acid. It is mobile, homogeneous liquid, colorless or slightly yellow, with an ester odour and the following structural formula:

$$\begin{array}{c} CH_3\\ |\\ CH-ONO_2\\ |\\ CH_3\end{array}$$

Isopropyl nitrate is sensitive to external impacts, is poorly soluble in water and is well soluble in alcohols such asesters, petrol, kerosene, acetone and benzene.

Isopropyl nitrate is hygroscopic; at low temperatures water dissolved in the product may become crystallized (see Table 3)

№	Feature	Norm
1	Density at 20 <sup>°</sup> C, gram per sm <sup>3</sup>	1,03- 1,05
2	Fractional mixture: - t <sup>0</sup> start of distillation, <sup>0</sup> C, no lower - 10% of product is to be distillated at t <sup>0</sup> , <sup>0</sup> C, no lower - 50% of product is to be distillated at t <sup>0</sup> , <sup>0</sup> C, no lower - 90% of product is to be distillated at t <sup>0</sup> , <sup>0</sup> C, no higher - 98% of product is to be distillated at t <sup>0</sup> , <sup>0</sup> C, no higher - volumetric part of the rest & losses, %, higher	98,0 99,0 100,5 106,0 108,3 2,0
3	Acidity, mg KOH per 100 ml of product, no more	2,0
4	Mass part of isopropyl nitrate, %, no more	0,1
5	Mass part of water, % no more	0,05
6	Mass part of mechanical admixtures, %, no more	0,01

*Table 3*, Technical requirements for isopropyl nitrate (OT-155)

Isopropyl nitrate is not corrosive with respect to aluminum and its alloys, mild, carbon and stainless steels. However, on long-term storage in humid conditions, it may be hydrolyzed. As a result, nitric and nitrous acids are formed and fuel becomes more corrosive, especially in contact with mild steels. That is why fuel must be kept in sealed tanks.

Fluoroplastics and high-pressure polyethylene (seals) are resistant to isopropyl nitrate. Fluorinated lubricants are most resistant among lubricants.

Such is chemical composition of components of rocket fuel: melanj, samine, isonite.

# TOXICOLOGY OF MILITARY HAZARDOUS WASTE—LIQUID ROCKET FUELS

#### Prof. Dr.-Ing. Wolfgang Spyra Brandenburg University of Technology, Cottbus Germany

- Abstract Throughout human history we have know that substances from the earth can bring helpful or harmful effects when ingested by humans. The fine line separating and pharmacon from a poison is dosage. This paper gives a brief introduction into the way the human body deals with toxic in take. Special attention is given to the components of binary and singular rocket fuel systems.
- **Keywords** Toxicology, eco-toxicology, contaminants, hazardous, human health, hygiene, samine, melanj, iso-propylnitrate, environmental health, dosage, symptoms of exposure.

## 1. INTRODUCTION

In order to send a rocket successfully to its target, it is necessary to release large quantities of energy in a relatively short span of time. Due to the propellants and components use during flight to assure that the target is reached, these rocket are extremely heavy. This report deals less with the components such as explosives or nuclear warheads such as chemical or biological weapons, rather it deals with rocket propellants, which are needed to carry the projectile to its target. Operating such a weapons system requires the careful physical handling of operational equipment and means of deployment, especially with the propellants. There are countless preparations connected to the launch of a rocket, which is to say there are many ways for operating personnel to come into contact with the dangerous rocket propellants. In the case of propellants, the dangers are twofold. Not only do the propellants hold a dangerously high energy potential, but the substances themselves also of have destuctive effects on safety equipment made of organic materials, and also on people, animals plants and micro-organisms. Non-organic safety equipment, water, soil and air may also be effected.

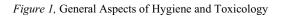
Since as early as the15<sup>th</sup> century humans have know that the classifying a material as a tolerable mixture, a medicine or a poison is merely a question of dosage. Theophrastus Bombastus von Hohenheim, better known under the name Paracelsus (1493-1541) taught the Latin phrase *dosis sola facit venenum*: only dosage makes the poison.

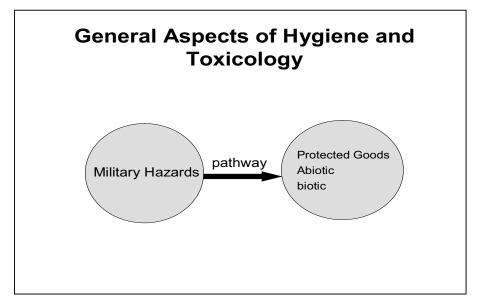
The simple principle coming from this knowledge tells us that every material is a poison, and that one must merely ingest enough of any substance in order for its effects become deathly. Far before Paracelsus' time, it was recognized that extracts from nature could have a healing effect on humans. These extracts had both plant and animal origins.

One way to illustrate this principle is by the example of cumarin. Cumarin is the active ingredient found in the woodruff plant. It is used as a taste enhancer in food but also a pharmicon and a toxin. Once in the human body, cumarin acts to thin the blood, and for this reason, it is successful when used against antithrombosis. This characteristic can help those with blood clots by releasing the clot in the blood vessels and improving their overall health. However, if the dosage of the drug is taken in higher concentrations, the blood in the body will become so thinned that the walls of the blood vessels, arteries and veins will be simultaneously penetrated. The result is that the blood no longer can be held in the vessels and leaks out, leading to death by internal bleeding. This tactic is still used by humans fight epidemics in animal herds.

All throughout human history, the pain-free life has been of the utmost importance. The human, a part of a whole system, is of the utmost importance when it comes to health and well-being. For this reason, occupation with the study of poisons has been of top importance to humans. The study of poisons has become known as toxicology. We know that we, as humans, are only a part of nature. To us, nature is our living space. It gives us the materials and products that we need to live: energy in the form of nutrition and water. Therefore, the ability to live a pain-free life depends on the quality of food and water available to us. Especially in the last 50 years, the understanding of the importance of nature to humans and their living space has grown. With the growth of human agglomeration in cities it becomes clear that large amounts of people produce large amounts of waste. This waste, through its own effects or through the effects of the substances as they change in nature, can lead to a damaging or even destruction of living space. We must learn that hygiene is necessary to enable a healthy co-existence. In relation to military means of operation and deployment the donator-acceptor system is structured in the

following presented areas: the genesis or source of the military contaminant, the transportation over the contaminated path, which first and foremost involves air and water, and the target object: humans. (See *Figure 1*: General Aspects of Hygiene and Toxicology).





According to this principle, hygiene is the study of the interruption of contamination transportation. This begins with the sealing off of the contaminant source, and continues to the interruption of the path of contamination transportation until the contaminant is kept from entering the organism and the individual is protected.

Many fields of toxicology have been created out of this knowledge. *Figure 2* gives an overview of the different areas and facets of toxicology. This report will discuss the human toxicological and eco-toxicological aspects related to the different dangers coming from liquid rocket propellants.

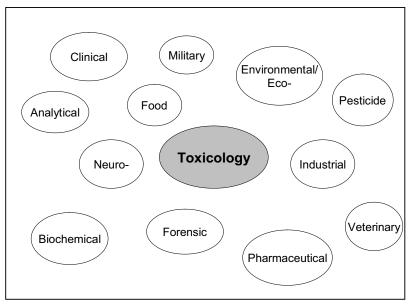
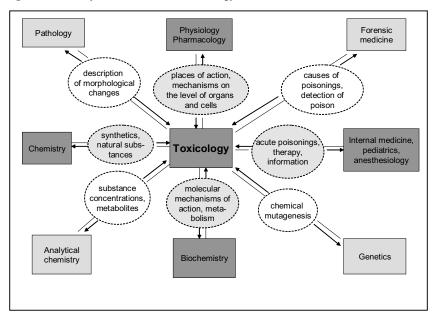


Figure 2, Fields of Toxicology

# 2. HUMAN TOXICOLOGY

There are many different roots to the conflict weather a material is poisonous or not. Therefore it is impossible to decide on just a single definition of this concept, but rather a diversity of definitions for "poison" seems more fitting.

*Figure 3* shows the diversity of interactions between toxicology and physiology/pharmacology, biochemistry, internal medicine, and chemistry. However, in the same way the reactions in question in the pathology square, between forensic medicine, analytical chemistry, and genetics may also be discussed.





In order to understand toxicological predecessors in the human body and to protect the human body from damages through ingestion of such toxins, it is important to know the uptake pathway of the toxic substance. This closer consideration limits itself here to the use of liquid rocket propellants. In order to be able to protect oneself from the consequences of such poisonous materials, one must identify the source of the contaminant. Only then is it possible to follow the pathway from the source, to the distributor, to the target object, and to humans as receivers of the contaminant. To protect oneself from incorporating contaminants into the human body, one must know the possible paths of uptake of the contaminant into the body.

The rocket propellants will here be described as melanj, samine and izonite. The chemical compositions of these liquids are known. The physical parameters for these liquids, such as the melting and boiling points, vapour pressure, density, viscosity etc. are also known. This information along with knowledge of environmental data such as the climate allows scientists to estimate the state of the material in different given environmental conditions. This estimation is especially important in understanding the contaminant pathway. The contaminant path explains the pathway that the toxic substance takes from the source to a target object, an organism.

The next important step is explaining the question of how a contaminant is able to enter the human body. There are, essentially, three ways that a considerable load of a toxin can enter the body: inhalation, oral uptake, or dermal uptake (see *Figure 4*).

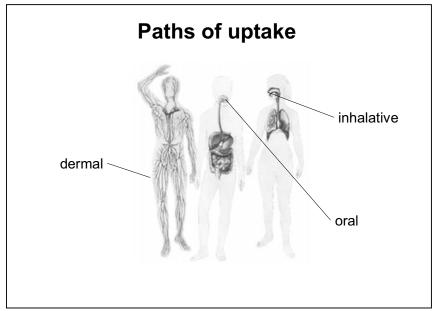


Figure 4, Paths of Uptake into the Body (Courtesy tooldoc.wncc.edu)

The human respiratory system is portrayed in *Figure 5*. The respiratory system is especially sensitive due to its structure and way of functioning. Since all inhaled materials, including contaminants, enter directly into the blood steam, inhaled toxins tend to have immediate effects on the body. The consequences of inhaling chemicals can be organic ailments or cellular damage. Damage to the highly sensitive alveoli and capillaries in the lungs is especially serious, because this sort of damage hinders healthy lung functioning by limiting inhalation volume.

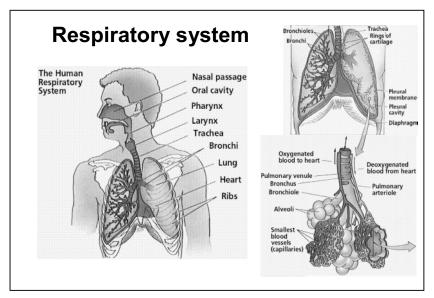
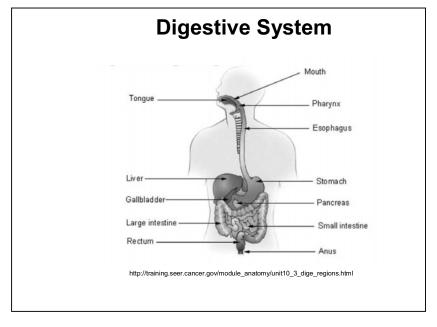


Figure 5, The Human Respiratory System (Courtesy tooldoc.wncc.edu)

Figure 6, The Human Digestive System (Courtesy training.seer.cancer.gov)



*Figure 6* shows the digestive system. It is also clear here that highly sensitive human organs are housed within the gastro-intestinal tract.

Though perhaps it seems to most unusual, that toxin uptake through the skin's surface is also possible. Without elaborating on medical abnormalities, the structure of the human dermas can be understood as having small blood vessels directly under the skin (see *Figure 7*).

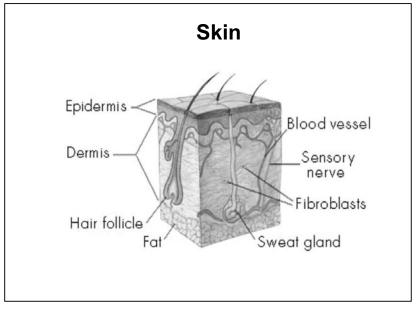


Figure 7, Human Skin (Courtesy tooldoc.wncc.edu)

These small blood vessels provide the body with localized access to life sustaining materials. Blood, however, is not intended to take up toxins and transport them to the body's different organs. Then toxins are take into the body, the blood itself can be damaged (Leukaemia), as well as the other organs of the body such as the liver and the kidneys. Direct harmful effects include: destruction of cells, damage to organs and respiratory problems. Indirect effects are mostly the result of serious damage to the body. These include: nausea, eczema, loss of hair and development of cancer and other diseases.

The biological processes of the human body are extremely complex. Explaining and interpreting these processes is the task of those in the medical field. However, those affected by the use of these chemicals should have a basic understanding of the ways contaminants can be transported into the

#### Toxicology of Military Hazards

human body. It is essentially the blood that takes over the transportation from "life to death." An easy way to understand the basic uptake of contaminants into the body is through the following classification. There are contaminants which largely appear dissolved in the aqueous system of the body (water-soluble) and there are others which tend to be found in the fatty tissues (fat-soluble). The effects of the contaminant depend on the type of solubility.

*Figure 8* gives an overview of the blood's function in the up-take of contaminants into the human body. The illustration lists the organs easily affected by the in-take of contaminants, however, all organs are known to be damaged by toxic substances.

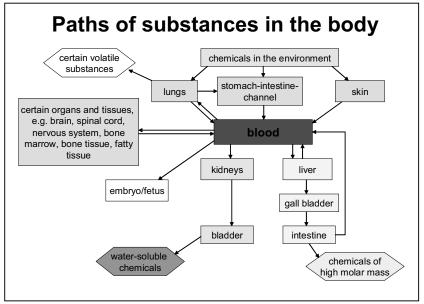


Figure 8, Substance Pathways in the Human Body

Luckily, there are safety measures which can be taken in order for those having regular contact with the toxins to avoid damaging effects. These safety measures deal with the civilian industrial handling. It is easy to imagine that in the military sphere the different nature of tasks demand a different set of safety measures. In time of peace it is, therefore, reasonable that the security regulations for civilian receive more attention. There are sufficient regulations determining the conditions, concentrations, and allowable exposure over a period of time. These regulations ensure that no sustainable danger in the sense of life-threatening damages occurs to the body's organs.

Only the most important protection concepts should be dealt with in directing the handling of toxic substances.

For the protection of persons who handle the chemicals on a regular basis, there are data which specify the concentration at which the effected person can be expected to remain without permanent damages even if they come into daily contact with the vapours of the chemicals. Of course these data are based on current scientific knowledge. These listed values are recognized by the German legal sphere as well as the legal sphere of the USA and that formerly recognized in the Soviet Union.

In the German Federal Republic the recognized legal evaluation system is the MAK-Value. This abbreviation stands for the *maximale Arbeitsplatzkonzentration* or the maximum workplace concentration.

The MAK-values were created in 1984 by the Commission for Evaluation of Hazardous Material of the German Research Association (DFG). The list was published as the Technical Rules Specified in Article 900 (TRgA 900). The MAK-values compare conditions to a standard of 20° C and 1013 milibars of pressure. Concentrations are given mostly in parts per million (ppm). A new list is published every year. The MAK-values apply to pure substances only, unless otherwise noted. The calculation of MAK-values for mixtures is produced by the DFG. In order to best understand the MAK-value system, the following demarcations are important.

- IIb: A substance, for which a MAK-Value has not yet been assigned.
- IIIA1: A substance with recognized carcinogenic potential.
- IIA2: A substance having carcinogenic potential in animal experiments under conditions comparable with workplace exposure.
- IIIB: A substance suspected of carcinogenic potential
- STUD: A substance under study

Comparable information is available for former USSR (PDK-values) and for the USA (TLV-values).

With the use of the US American evaluation system there are additional specifications which serve as a useful supplement to the German system. Following are some important demarcations.

TLV-TWA:	Time weighted average
TLV-STEL:	Short term exposure limit
TLV-c:	Ceiling

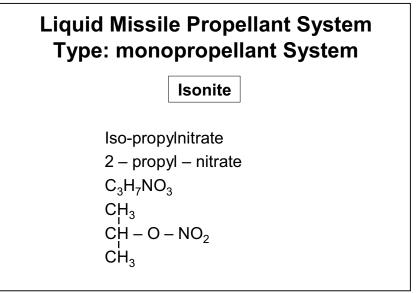
These additions carry different factual calculations. Different toxins may be emitted in different levels, depending on the potency of the source. The variations can be integrally recorded in order to be able to record the total accumulated mass of the toxin. It is important that the critical values are not exceeded at any time during the handling of the toxin. This would, in essence, constitute a lethal dosage. Depending on the toxin in question, humans may be able to take in a higher level of a substance without incurring long-term health maladies if exposure is kept to a shorter period of time.

The TRD-value (tolerated adsorbed dosage) can also be called upon as a standard human toxicological evaluative tool. Corresponding to its definition, derivations of its data and the protective measures set up by the data from the World Health Organization, the TRD-value provides the level of daily dosage that one could sustain over a lifetime of exposure without inducing negative health impacts.

# 2.1 **Operational Materials**

Here the operational materials of two different combustion principles will be discussed. One is the singular system, in which application is preformed using only one fuel. In the rocket motor only one component is fed-in for combustion. The second propellant system is a binary material mixture which is fed into the rocket motor and then brought to ignition. The single component propellant is composed of the fuel with common name isonite. Chemically seen, it is iso-propylnitrate (see *Figure 9*).

Iso-propylnitrate is highly soluble in water and is toxic to humans when inhaled, ingested, or absorbed through the skin. Vapour and mist irritate the eyes, mucous membranes and upper respiratory system. Skin irritation and cyanosis may occur as a result of absorption in blood. Exposure can cause nausea, dizziness, headaches, blurred vision and heart palpitations. The natural microbial degradation of isonite may form nitro samines in the body. This substance is thought to cause cancer, however further evidence is not available. Figure 9, Iso-Propylnitrate (Isonite)



This observation leads further to the supposition that since isonite is highly water-soluble and has a high vapour pressure, the levels of contamination of the water and air in the storage areas are of heightening concern. For this reason, secure conditions and limited handling of isonite in prolonged storage is vital. In addition, for security reasons, and since isonite is an explosive, certain modes of transportation must be forbidden.

When isonite is released into the environment, the environmental conditions play a role in determining the amount of time the chemical stays present in the environment. In the same way, environmental conditions also affect the overall effects the chemical will have on the ecosystem it enters. Nitro compounds exposed to environmental influences are subject not only to transformation through hydrolysis and oxidation. There could very well also be microbiological reactions taking place. It is well known that nitro groups can be reduced to amine and on the way pass through stages of nitro samines. Nitro samines are *a priori* suspicious compounds because a majority of these compounds are proved to cause cancer in humans, or are thought to have this potential.

If these chemicals reach humans, weather through dilution into water sources or through the food chain, the health risks cannot be out ruled. Only acute

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symptoms can probably be avoided. The answer to this question has already been given to us by Paracelsus.

When isonite is used as intended, to place a rocket into flight, the same sorts of environmental problems are generated with polluted water and carbon dioxide, carbon monoxide and nitrose gases emissions. Acid rain and acidified soil and water are the products.

The binary system consists, as the name suggests, of two propellant components: the oxidizer and the source of energy. The operation materials are melanj, the oxidizer, and samine, the source of energy.

The composition of these chemicals is depicted in *Figure 10*. There are actually three different types of oxidizer and only one type of source of energy, with the designation samine.

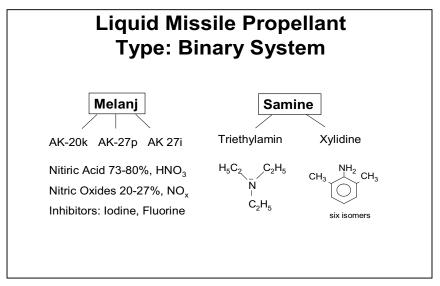


Figure 10, Liquid Missile Propellants: Binary System

The three oxidizer components differ in the amounts of the ingredients and inhibitors. These values are also found in *Figure 10*. Inhibitors and additives are meant to stabilize the mixed system. In the case of melanj storage, the additives such as iodine or fluoride components function to inhibit the process of corrosion. One can easily see that the strength of the walls of the storage containers used to hold malanj varies. Where the walls of the storage tank are covered with a layer of the fluid mixture of nitric acid with dissolved nitrogen

the thickness of the tank walls can be up to 30 mm. Where the tank walls have contact with the material in its gas phase, however, the thickness of the walls can be measured to be less than 1mm. The reason for the higher rate of corrosion in the gas phase lies on the absence of inhibitors.

Samine is composed of a mixture of two materials: triethylamine and xylidine. Xylidine is a technical product with a six isomer compound. The combination of the two chemicals, melanj and samine, in the rocket motor ignites the samine mixture without needing any additional source of ignition.

## 2.2 Sources of Data

There are still even more substances used as operational materials. We look to scientific literature to better understand the physical, chemical and biological data necessary for an evaluation of the dangers of the chemicals in relation to different organisms (biotic resources) and the state of the environment (abiotic resources). However, the availability of such information is not always available. In most cases, what is readily available is the physical data: the chemical structure and the environmental evaluation. The sources of data for biological information are, unfortunately, unsatisfactory.

## 2.2.1 Iso-Propylnitrate: C<sub>3</sub> H<sub>7</sub> NO<sub>3</sub>

The data available on iso-propylnitrate are shown in *Figure 11*. From the physical date, molecular weight, melting and boiling points, as well as the density and the relative vapour pressure of VP=40 mbar, we can see that this compound is very mobile under normal conditions (p=1,  $T=25^{\circ}$  C). Even at room temperature the chemical is easily evaporated. Therefore, hazardous conditions can easily be created when isonite is stored in a closed room or warehouse with limited fresh air flow. Here, the dangers of inhalation or skin absorption would be severe. An Oktanol/Wesser Coefficient, which estimates the behaviour of a chemical once it is in the human body, is not known for isonite. According to the solubility information, isonite is also easily absorbed into the human body. Toxicological data such as lethal dosage, MAK-values, or TRD-values, are not available in this case, but it is ascertained that acute effects may be suffered though inhalation, ingestion or skin absorption of vapours or mist.

Figure 11, Iso-Propylnitrate Chemical Data

2				ta She -propy	eet Initrate)	)	
Name	Formula	MG	Melting point [°C]	Boiling point [°C]	Density [g/cm³]	V <sub>p</sub>	K <sub>ow</sub>
2-propynitrat iso-propynitrat	C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	105,1	-82	101-103	1,047 @ 15,5°C	40 mbar	n.a.

#### 2.2.2 Nitric Acid: HNO<sub>3</sub> and NOXE: NO<sub>2</sub> N<sub>2</sub>O<sub>4</sub>

The nitric acid and the nitrogen oxide belong to the group of compounds, about which adequate information is available. The most relevant information is found listed in *Figure 12*.

Since nitrogen oxide always converts to nitric acid when mixed with water under normal atmospheric conditions, and because nitric acid is always miscible with water, any contact with living beings could result in the spread of the chemical into the body. Accordingly, a high concentration of the chemical in the body will destroy cell tissue or carry nitrates into the bodily fluids. In the sense of toxins, nitric acid is considered a hazardous substance. One of the most important properties of nitric acid is that in higher concentrations, or as melanj, it reacts with and causes spontaneous ignition of organic substances such as wood shavings sawdust, cotton, cellulose and, of course, samine.

lame	Formula	MG	Melting point	Boiling point	Density	V <sub>p</sub>
Nitric acid	HNO <sub>3</sub>	63,01	[° <b>C]</b> -41,6	[° <b>C]</b> 83	[g/cm <sup>3</sup> ] 1,50 @ 25°C	7,3mbar
Nitric tetraoxide	N <sub>2</sub> O <sub>2</sub> /NO <sub>2</sub>	46,01	-11,3	21,1	1,45 @20°C	1,6 bar

Figure 12, Chemical Data Sheet for Melanj

Reactions of nitric acid may be different, depending on concentration. For nitric acid concentrations greater than 70% there is a danger of fire when it comes in contact with flammable substances. It also causes severe burns. One should not inhale the vapours, and in case of contact with the eyes, one should flush the eyes with water and call a physician. Protective clothing are required at all times when working with the chemical. Even concentrations of between 20% and 70% are strong enough to cause severe burns. This concentration should be kept away from children. The vapours should not be inhaled, and in case of contact with eyes, follow the same procedure as above. Any contaminated or saturated clothing should be removed and cleaned. It is crucial to remember never to add nitric acids to water or water to the acid. This is, after all, an exothermic reaction.

#### 2.2.3 Samine

As described above, samine is a mixture of triethylamine and xylidine. There are currently six known isomers of xylidines. Therefore, one must discuss the physical properties of a mixture of seven compounds. The physical data about samine are shown in *Figure 13*.

				el Ja	mine	
Formula	MG		Boiling point [°C]	Density	V <sub>p</sub>	K <sub>ow</sub>
		[°C]		[g/cm <sup>3</sup> ]		
C <sub>6</sub> H <sub>15</sub> N	101,2	-114,7	89,3	0,7255 @ 25°C	72 mbar @ 20°C	1,45
C <sub>8</sub> H <sub>11</sub> N	121,18	-15 up +51	214 up 220	0,979- 1,075	6-8 mbar	Not available
	C <sub>6</sub> H <sub>15</sub> N	0 10	point         point         [°C]           C <sub>6</sub> H <sub>15</sub> N         101,2         -114,7           C <sub>8</sub> H <sub>11</sub> N         121,18         -15 up	point         point         point         coint         cent         cent <thccn< th="">         cent         cent         &lt;</thccn<>	point         point         point         [°C]         [g/cm³] $C_{6}H_{15}N$ 101,2         -114,7         89,3         0,7255         @ 25°C $C_{8}H_{11}N$ 121,18         -15 up         214 up         0,979-	point         point <t< td=""></t<>

Figure 13, Chemical Data Sheet for Samine

The difficulty of judging the danger of these mixtures lies in problem that confirmed knowledge is only known about the individual parts of the mixture, and not specifically for the mixture as a whole. Since the mixture may have different qualities than the individual parts, the characteristics of the individual parts cannot be simply applied to the mixture. In order to securely judge the level of danger, one must design a scenario where the desired data can be calculated using already known information. This requires additional intensive experimentation. Parts of this data may be readily available from the military sector. The known data about vapour pressure suggests that samine is very mobile in storage conditions. Because of this characteristic it is important to prevent leakage of samine from tanks. As an organic substance, it has the ability to break up and dissolve plastic coatings and rubber. This characteristic of this mixture must be watched very carefully, especially in storage conditions. One advantage of this light yellow to brown chemical, is that in the case of leakage or improper storage causing release of the chemical, one can easily sense organoleptically the classic odour common to the amine group. Only the toxicological data for microsomal mutagenicity on Salmonella typhimuim, lethal dosage, LD50 and MAK-value are available (see Figure 14).

Figure 14, Toxocological Data for Xyidines

	Microsomal mutagenicity on Salmonella typhimurium, µmol/plate	LD <sub>50</sub> , rat oral mg/kg
2,3-Xylidines	5	836
2,4-Xylidines	1	467
2,5-Xylidines	10	1297
2,6-Xylidines	50	707 <sup>b</sup>
3,4-Xylidines	5	812
3,5-Xylidines	1 <sup>a</sup>	707
<sup>a</sup> mg/plate. <sup>b</sup> Mou	se	

# 3. ECO-TOXICOLOGY

The eco-toxicology is measured in relation to the effects of toxic substances on abiotic elements of the environment such as water, soil, and air. In order to distinguish the natural balance of stabilities and instabilities, this evaluation deals with the anthropogenic elements of nature. Human beings extract and consume natural resources to the point where the quantities and characteristics of the natural resources are put into question. The balance is either disturbed or destroyed. It is the task of science to recognize these changes and to determine what can be done to avoid continued degradation or to heal the damage that has already occurred. Therefore, a part of eco-toxicology is environmental health.

From the physical, chemical and biological characteristics one can determine the behaviour of a substance. In some cases, these characteristics can also provide clues as to a substance's environmental behaviour.

Iso-propylnitrate is a compound that can be decomposed microbiologically in the environment. Since it is composed of a compound including a nitro-group,

#### Toxicology of Military Hazards

it follows that it has the possibility to produce nitro samine as a product of its decomposition, which, as mentioned above, is thought to cause cancer.

As for the oxdizer melanj, a release of this material leads to evaporation of nitrogen oxide. Together this reacts with the moisture in the air and the available oxygen to form nitric acid. When nitric acid is taken into the water cycle, it falls as acid rain. The consequences of such acid rain are already widely known. Comparative consequences are also known for nitric acid at extreme dilutions.

Nitric acid in high concentrations must be considered severely dangerous. It is already recognized that the nitric acid based oxidizer melanj can ignite and cause fire in organic materials without the help of outside influences. But what is even more significance, is that besides the destruction of organic materials, melanj can also dissolve non-organic materials such as metals and metal oxides.

There is no eco-toxicological information available in scientific literature for triethylamine. In the case of xylidine, however, there is substantial environmental information. Xylidine is expected to have a high to medium solubility in soil. Due to the high reactivity of the aromatic amino groups, anilines are expected to strongly absorb the aromatic humus or organic matter in the soil. Since xylidines have a low vapour pressure they tend to strongly bind with suspended organic matter. Experimental data suggest that xylidines might biodegrade under aerobic conditions in soil and water. Given such characteristics, it is especially important to conduct long-term monitoring of humus and organic matter contaminated by releases of samine. Fortunately, xylidine will eventually be dissolved through a natural self-cleaning process in which the microbiology in connection with the ambient oxygen consumes the pollutant.

Considerations for danger assessment must be based on an expanse of possible means of contaminant assessment. The transport media air and water offer the largest dangers. Compounds with a high vapour pressure or mobile particles of solid matter, such as contaminants and dust or fine sand can be spread by adequate wind movement. Substances able to be dissolved in water, are taken-up by rainwater and are dispersed into surface or underground water movement.

The considerations for danger assessment must always differ for each contaminant or for every mixture of contaminants.

# LOCATION OF LIQUID MISSILE PROPELLANT DEPOTS IN AZERBAIJAN, RECENT STORAGE STITUATION, AND RISK ASSESSMENT

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Abstract The storage of liquid missile propellants, namely Melanj (oxidizer consisting of nitric acid and nitrous oxides), Samine (mixture of equal parts of xylidine and triethylamine) and Isonite (isopropyl nitrate) in Azerbaijan is discussed in this paper. Recent storage conditions, the amounts of chemicals stored, the environmental factors and human geography at the two major storage facilities and chemical properties of the substances are combined for a preliminary risk assessment. Recommendations of necessary actions with respect to public and environmental safety are given.

# **1. INTRODUCTION**

The end of the Cold War in the early 1990s and the disintegration of the former Soviet Union have left many military facilities, equipment, sites, substances, and materials unused. For more than 10 years, these substances, facilities and sites are have been subject to conversion.

Conversion is defined as a transformation from military to civilian uses. Examples include the destruction of arms and ammunition through material recycling, the clearance ammunition and UXOs from military sites in order to create usable land, the disassembly of unused military installations, and the re-development of former barracks as living and business areas. Conversion involves the destruction of military capabilities according to international agreements as well as the environmentally compatible disposal of hazardous substances and ammunition.

In the past, however, conversion was often synonymous to inactivity. When arms, equipment, materials, substances and sites were no longer needed for military purposes, demilitarization often meant that they were deposited or

left where they were at the time they became redundant. This is true not only for the former Warsaw Pact countries but also for any other country in the world conducting, which most countries were after 1990.

The problem of abandoned liquid ballistic missile propellants in Azerbaijan, the subject of this NATO Advanced Research Workshop, is only one example of the problems of public safety brought on by conversion.

In this report, the present situation at the two major storage sites for liquid ballistic missile propellants in Azerbaijan, near the towns of Alyat and Mingechevir, will be presented and discussed along with a preliminary risk assessment. This report is based on information supplied by the Azerbaijan Ministry of Defence (MOD) and NATO Supply and Maintenance Agency (NAMSA) on the levels of liquid ballistic missile propellants and by site inspections at two storage facilities conducted on 1 October 2003 (Alyat facility) and 3 October 2003 (Mingechevir facility). These two facilities must be viewed in the context of their surrounding geography and their environments.

According to information made available by the Azerbaijani MOD, liquid ballistic missile propellants (fuels and oxidizers) that are no longer used by the Azerbaijani Armed Forces are stored at two major sites (military supply installations at Alyat and Mingechevir) and one or more branch storage sites [Mission of Azerbaijan to NATO] in the following quantities:

- Oxidizer: 1,400 metric tons of AK-20k, AK-27p, AK27i Oxidizers (73-80% nitric acid and 20-27% nitric oxides with iodine or fluorine inhibitor.
- Fuels: 450 metric tons of TQ-02 Samine (50% triethylamine + 50% xylidine)25 metric tons of OT-155 Isonite (isopropyl nitrate) An unknown quantity of TM-185 (20% gasoline + 80 % kerosene)

Since the disintegration of the Soviet Union with the withdrawal of Soviet troops from Azerbaijan and the formation of national armed forces, these chemicals have been virtually "abandoned". Even though they are still stored on military bases and guarded by military staff, there is obviously no interest in a military use and no means for safe storage and handling of these chemicals.

For all stored chemicals leakages are given. Due to their aggressiveness in combination with water, oxidizers in particular are continuously leaking into the atmosphere and to the soil. The oxidizers are corroding stainless steel as Location of Missile Fuel Component Storage Sites and Risks

well as aluminium storage tanks. Leakage of oxidizers is obviously due to macroscopic leaks in tanks. Traces of leakages on the soil (oxidation of soil iron the brownish Fe(III)), yellowish-brown plumes of nitrous gases escaping from the tanks and a characteristic smell on the storage sites are observed. The leakage of TQ-02 Samine, OT-155 Isonite and TM-185 is mainly detected by organoleptic means due to a strong characteristic smell at both inspected storage sites.

The detailed description of the two inspected storage sites is given subsequently.

# 2. SITUATION AT ALYAT DEPOT

Alyat is a town of approximately 20,000 inhabitants (estimated). It is situated approximately 75 kilometres southeast of Baku at the shoreline of the Caspian Sea. The main road from Baku to the south of the country and to Iran as well as the two major rail tracks to Georgia and the Naxivan exclave lead through Alyat.

A military depot for all kinds of fuels (diesel, kerosene, gasoline, liquid missile propellants, etc.) is situated in the southwestern outskirts of Alyat. The distance to the nearest residential area is approximately 350 metres. Sensitive installations such as schools and hospitals are situated within a perimeter of 500 meters from the depot.

Besides fuels, lubricants, and other chemicals that are supplied to armed forces units from the depot, a large quantity of liquid ballistic missile propellants is stored in a separated section of the depot. According to an inventory of the stored chemicals on behalf of the Azerbaijani MOD the following types and amounts are stored at Alyat (as of January 2003):

1,028 metric tons of oxidizers (AK-20k, AK-27p, AK-27i) 155 metric tons of Samine (TQ-02) 100 kg of Isonite (OT-155)

The oxidizers are stored in 22 tanks with a volume of 40 - 50 cubic metres each. Several tanks show severe leaks such as corroded safety valves, broken welding seams, wholes due to corrosion of the tank metal plates and wholes at the bottom of the tank due to pressure from underlying stones. However, due to the documented leakages, many of the tanks appear to be empty. Traces on the soil surfaces and concrete barriers surrounding the tanks indicate that several leakages with major releases of nitric acid/nitric oxides occurred

recently. Concrete barriers show severe weathering (probably due to contact with nitric acid) and the bare soil around the tanks often appears wet or rustybrown, obviously due to oxidation of Fe(II) to Fe(III) by nitric acid. Even where tanks appear to be almost empty, yellowish-brown fumes escaping from valves or leaks indicate an ongoing atmospheric release of nitrous gases. According to the MOD of Azerbaijan, the on-site underground storage facilities (earth-covered shelters) do not contain any oxidizer. According to this information, the oxidizers where removed from the underground storage facilities because no personal protection equipment (respiratory masks, filters, protection suits, gloves, boots) were available – thus making the handling of oxidizers in underground storage facilities impossible. Examples for leaks and leakages are shown in the photo documentation.

In addition to the 22 storage tanks, four rail tank cars are stabled on the site. According to the Azerbaijani MOD, the tank cars will be still suitable for transport purposes after an intensive overhaul. Rail tracks that might also need overhaul before use for transportation connect the depot with the main railway route Baku – Georgia and Baku – Naxivan Exclave. Approximately 70 small tanks (6 m<sup>3</sup> each) are available for transportation and emergency response purposes.

Until recently, ammonia used as a neutralizing agent for the oxidizers, was available at the Alyat depot. However, with the latest spills, the ammonia supplies have been exhausted. Recent prevention and emergency response at the depot with respect to leakages of oxidizers is thus restricted to the cutting of vegetation and ploughing of the soil in the vicinity of the oxidizer storage tanks (in order to prevent any contact of the oxidizer with flammable material) and - in case of a major leakage - pumping the oxidizer into the small storage containers that are available for emergency response.

Samine, a mixture of 50 % triethylamine and 50 % xylidine, is stored in conditions similar to that of the oxidizers. Approximately 15 tanks with a volume between 10 cubic metres and 50 cubic meters each are kept separately (distance circa 100 meters) from the oxidizers. Like the oxidizer tanks, the tanks are lying on the bare ground without any stand, rack or catchment basin for leakages. A strong characteristic smell of xylidine and triethylamine indicates leakages. However, no macroscopic leaks are visible on the tanks. In contrast to the oxidizer tanks which are made from stainless steel or aluminium, the Samine storage tanks are made from steel and thus are - despite the arid climate - subject to corrosion.

Isopropyl nitrate, of which only 100 kg are reportedly stored at the Alyat depot, is kept in a separate shed. Infrared footage of the ten barrels indicates

Location of Missile Fuel Component Storage Sites and Risks

that these are leaking as gas plumes seem to be emitted from the barrels from time to time.

The groundwater table depth at the Alyat storage site is not precisely known. However, according the Azerbaijani MOD, no groundwater use is known in the vicinity and despite the vicinity of the Caspian Sea the groundwater is believed to be at a depth of approximately 40 metres below the surface confined beneath an impermeable layer.

A branch of the Alyat depot that was not visited (approximately 15 km from the main depot) also holds stockpiles of both oxidizers and Samine, according to information by the Azerbaijani MOD.

# 3. SITUATION AT THE MIGECEVIR DEPOT

Mingechevir is a town of approximately 100,000 inhabitants (estimated). It is situated approximately 275 kilometres east of Baku at the Kura river and the Mingechevir reservoir, a huge freshwater reservoir. The main road from Baku to Ganca and Georgia as well as the major rail track to Georgia (used for oil export) pass Mingechevir.

A military depot for all kinds of fuels (diesel, kerosene, gasoline, liquid missile propellants, etc.) is situated approximately 20 kilometres south of Mingechevir, about 500 m from the main railroad to Georgia. The distance to the nearest residential area is approximately 500 metres. Sensitive installations such as schools and hospitals are situated within a perimeter of 1,000 meters from the depot.

Besides fuels, lubricants, and other chemicals that are supplied to armed forces units from the depot, a large quantity of liquid ballistic missile propellants is stored in a separated part of the depot. According to an inventory of the stored chemicals on behalf of the Azerbaijani MOD the following types and amounts are stored at Mingechevir (as of January 2003):

380 metric tons of oxidizers (AK-20k, AK-27p)290 metric tons of Samine (TQ-02)24 metric tons of Isonite (OT-155)

The oxidizers are stored in about 15 tanks, mostly lying on the bear ground as in Alyat. Leaks and traces of spills similar to those in Alyat were also clearly visible. Because no large backup tanks for emergency response are available,

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during the last leakage, oxidizer from a static tank was pumped into a single rail tank car standing on the site. All tanks including the rail car show severe corrosion and leakage. Safety valves have typically corroded away from the tank inspection holes. In contrast to the Alyat depot, the storage at Mingechevir seems to have always relied on storage in surface-tanks and not in soil shelters. Nevertheless, two tanks were covered with soil. Preventive measures are restricted – as for the Alyat depot – to the cutting of vegetation and ploughing of the soil in order to prevent organic (flammable) material in the vicinity of the oxidizer. For emergency response purposes (oxidizer neutralization), seventeen cubic meters of ammonia are available in a tank situated within the range of the oxidizer storage tanks. The ammonia is frequently used to neutralise spilled oxidizer, yielding ammonia nitrate. Pumps and approximately 170 backup containers (similar to the six cubic meter containers seen in Alyat) for the oxidizer are also available.

The storage facility for the approximately 240 metric tons of Samine is situated in a pit that is approximately 2.5 metres deep, 100 metres long and 20 metres wide. Because the groundwater level is only about 1.0 and 2.0 metres below ground surface, the tanks are lying in the open groundwater in the pit. Water level traces on the tank walls show that the water level is variable over time. Together with the Samine, an unknown quantity of TM-185 fuel (80% kerosene, 20% gasoline) is stored in tanks in the same pit. A strong characteristic smell and floatings on the water are evidence for leakages from the tanks. Due to the construction material of the tanks (steel), severe corrosion is evident where the tanks have been exposed to water. Dark-red to violet colouring of large areas of the soil surrounding the storage pit point to larger spills of Samine in the past. It is known that Samine spills on soils yield a violet to dark-red colour of the soil, probably due to a chemical reaction of triethylamine cations with soil constituents. According to the deputy commander of the depot, no backup tanks, pumps, neutralising agents or personal protection equipment for the handling and/or emergency response with respect to Samine is available.

Isopropyl nitrate (24 metric tons) is stored in sheds that are situated at a distance of about 50 metres and 150 metres from the samine/TM-185 storage pit and the oxidizer storage tanks respectively. A strong characteristic smell inside the Isonite storage shed, similar to that of isopropyl alcohol, gives evidence for leakages from the Isonite barrels.

On inquiry, the deputy commander of the depot declared that no means for emergency response are available with respect to isopropyl nitrate.

# 4. RISK ASSESSMENT

The risk assessment is subdivided into two parts. The first part considers the properties of the chemicals in question (nitric oxides, triethylamine, xylidine, isopropyl nitrate), while the second part considers the chemicals with their respective properties in the situation of the two storage sites at Mingechevir and Alyat.

# 4.1 Properties of Chemicals in Quesiton

## 4.1.1 Oxidizers

The oxidizers that are referred to as "Melanj" or with their military codes AK-20k, AK-27p, and AK-27i are all compositions of nitric acid and nitric oxides with different additives and inhibitors such as iodium or fluorine. The content of nitric acid is 80 % for AK-20k and 73 % for AK-27i and AK27p.

## 4.1.1.1 Nitric Acid (HNO<sub>3</sub>)

- Colour/Form: Colourless, yellow or red, fuming liquid.
- Odour: Characteristic acrid to sweet odour.
- CAS-No. 7697-37-2
- Melting point: 41.6°C
- Boiling point: 83 °C
- Density: 1.55 g/cm<sup>3</sup> @ 15.5°C
- Vapour pressure: 63.1 mm Hg @ 25 °C = 8,412.5 Pa
- Solubilities: Miscible with water, soluble in ether
- Corrosivity: In presence of traces of oxides nitric acid attacks all base metals except aluminium and special chromium steels.
- Environmental Fate: If released into the environment, nitric acid will be dissoluted by soil water, surface water and/or groundwater. Hydronium ions will be neutralized by carbonate minerals and thus be eliminated quickly. However, larger spills may result in the (local) solution of soil material and acidification of water resources. Nitrate ions will remains in the water for longer periods and may contribute significantly to eutrophication. Transport with (ground)water flow has to be considered significant because no hindrance is to be expected.
- Fire: Nitric acid is not combustible, but will react with water or steam to produce heat. Contact of concentrated nitric with combustible materials may increase the hazard from fire and may lead to an explosion.

• Human Toxicity: Contact with nitric acid or inhalation of nitric acid fumes will result in severe cauterisation of skin, mucous membranes, the respiratory system (pulmonary oedema) and eyes.

## 4.1.1.2 Nitric Tetroxide (N<sub>2</sub>O<sub>4</sub>)

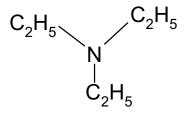
- Form/Form: Colourless gas, below 22 °C yellow or colourless liquid.
- Odour: Odourless gas.
- CAS-No.: 10544-72-6
- Melting point: 9.3°C
- Boiling point: 21.15 °C
- Density: 1.45 g/cm<sup>3</sup> @ 20 °C
- Vapour pressure: 646 mm Hg @ 25 °C = 86,124.7 Pa
- Solubilities: not applicable (gas)
- Corrosivity: Corrosive liquid.
- Environmental Fate: Due to high vapour pressure, only atmospheric pathway is relevant. Quick dissolution in ambient air. However gases are heavier than air and will spread along ground.
- Fire: Does not burn itself but will support combustion as a strong oxidising agent. May ignite combustibles (wood, paper, oil, clothing, etc.), containers may explode when heated, ruptured cylinders may rocket.
- Toxicity: Inhalation of nitric tetroxide fumes/gas will result slowly evolving but progressive inflammation of lungs. Will impair gas exchange and lead to cyanosis. in severe cauterisation of skin, mucous membranes, the respiratory system (pulmonary oedema) and eyes.

## 4.1.2 Samine

Samine is a mixture of 50 % triethylamine and 50 % xylidine. It is used as a fuel for ballistic and air defence missiles.

# 4.1.2.1 Triethylamine (C<sub>6</sub>H<sub>15</sub>N)

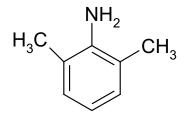
- Colour/Form: Colourless liquid.
- Odour: Strong, ammoniac to fishy odour.
- CAS-No.: 121-44-8
- Melting point: 114.7 °C
- Boiling point: 89.3 °C



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- Density: 0,7255 g/cm<sup>3</sup> @ 25 °C
- Vapour pressure: 57.1 mm Hg @ 25 °C = 7,612.5 Pa
- log K<sub>OW</sub>: 1.45
- Solubilities: Soluble in ethanol, oils and ethyl ether, very soluble in acetone, solubility in water 15,000 mg/l 20,000 mg/l (@20 °C/65 °C)
- Corrosivity: Liquid triethylamine will attack some forms of plastics, rubber, and coatings.
- Environmental Fate: Due to a high vapour pressure, triethylamine will solely exist as vapour in the ambient atmosphere and will be degraded by hydroxyl radicals (photochemically produced) with a half-life of four hours. Due to a pKa of 10.78, triethylamine will mainly exist as a cation if released to soil or water and therefore strongly adsorb to organic carbon and clay (in soil). Based on screening tests, biodegradation of triethylamine will not play a relevant role in the degradation of triethylamine. Because of a low log K<sub>OW</sub>, biodegradation will not occur.
- Fire: Triethylamine is a flammable/combustible material that may be ignited by heat, sparks of flames. Vapours are heavier than air and form explosive mixtures with air. Vigorous reaction with strong acids.
- Toxicity: Mainly local effects. Eye irritant eye contact causes severe burns. Clothing wet with triethylamine will cause skin burns. Carcinogenic (skin), temporary blue hazy vision due to exposal to ethylamines, vapours irritate nose, throat, lungs, causing coughing, choking an difficult breathing.

#### 4.1.2.2 Xylidine (C<sub>8</sub>H<sub>11</sub>N – six isomers)



- Colour/Form: Pale yellow to brown liquid above 20 °C.
- Odour: Weak aromatic amine odour.
- CAS-No.: 1300-73-8
- Melting point: 36 °C
- Boiling point: 213 226 °C
- Density: 0.97 0.99 g/cm<sup>3</sup>
- Vapour pressure: 0.028 0.015 mm Hg = 3.7 20 Pa
- log K<sub>OW</sub>: not available
- Solubilities: Slightly soluble in water, soluble in alcohol and ether.
- Corrosivity: Liquid xylidine will attack some forms of plastics, rubber, and coatings.
- Environmental Fate: Xylidines are expected to have a high to medium solubility in soil even though anilines are expected to adsorb strongly to humus or organic matter in soil due to the high reactivity of the aromatic amino groups. Due to low vapour pressures, xylidines are not expected to occur in vapour phase or to volatilize from soil or water. In water, xylidines might strongly adsorb to suspended organic matter. Experimental data suggest that xylidines might biodegrade under aerobic conditions in soil and water.
- Fire: Xylidines are flammable/combustible substances that may burn but do not ignite readily. When heated, vapours may form explosive mixtures with air. Contact with metals may evolve hydrogen gas.
- Toxicity: Possibly carcinogenic, intoxication may result in headache, dizziness, cyanosis.

## 4.1.3 Isopropyl Nitrate (2-propyl nitrate, C<sub>3</sub>H<sub>7</sub>NO<sub>3</sub>)

Colour/Form: Colourless liquid Odour: Isopropyl alcohol like odour CAS-No.: 1712-64-7 Melting point:  $-82^{\circ}$ C Density: 1.047 g/cm<sup>3</sup> @ 15.5°C Vapour pressure : 40 mm Hg = 5,332.8 Pa Flash Point: 13 °C Solubilities: Probably highly soluble in water Environmental Fate: no data available Fire: Highly flammable, self-ignition possible when in contact with organic material, explosive. Toxicity: no data available

# 4.2 Risk Assessment of Storage Sites

#### 4.2.1 Situation at the Alyat Depot

The situation at the Alyat depot has to be considered less dangerous than at the Mingechevir depot.

The main hazard at Alyat is posed by the oxidizers that are stored in leaky tanks with continuously ongoing leakage and occasional larger spills. As no neutralizing agents, personal protection equipment, pumps etc. are available, immediate action to provide the necessary emergency response equipment is essential to prevent further leakages of nitric acid and nitric oxides.

The storage conditions for Samine are insufficient. Despite leakages, made obvious by a strong characteristic amine odour in the vicinity of the Samine tanks, and, because of the dry climate and non-corrosivity of Samine against steel the storage can be considered relatively safe on a scale of several months to a maximum of two years.

The quantity of isopropyl nitrate stored at the Alyat facility is low (approximately 100 kg). However, uncontrolled detonation of the isopropyl nitrate after self-ignition of the leaking barrels could result in larger damages if the Samine and oxidizer storage facilities are affected during such an accident.

Major leaks or spills of nitric acid and nitric oxides as well as Samine would pose severe hazards for the local civil population living in residential areas only 350 metres from the storage site. Schools and hospitals could also be affected.

#### 4.2.2 Situation at the Mingechevir Depot

The situation at the Mingechevir depot must be considered more critical. The main threat here is posed by heavily corroded tanks filled with Samine and TM-185 that are situated in a pit directly in contact with the groundwater. Here, organoleptic observations (strong characteristic Samine odour, dark-red to violet soil) indicate recent and ongoing severe leakages of triethylamine and xylidines into the environment. Due to the high solubility of triethylamine in water (15 - 20 g/l) and the storage of tanks in contact with groundwater, the ongoing contamination of huge groundwater quantities close to a major drinking water reservoir of the Republic of Azerbaijan is almost certain.

Residents living close to the depot regularly notice the odour of Samine and oxidizers but have not yet protested against the situation. However, due to a small distance between the depot and surrounding civil population, effects on the population during a major accident (spill or leakage) are likely. It is not known whether people in the surrounding residential areas use groundwater from wells as drinking water or process water.

The fact that no emergency response equipment (personal protection equipment, pumps, backup tanks, neutralising agents, etc.) except one normal fire truck is available urges immediate action with respect to the Samine problem at the Mingechevir depot.

The oxidizer (nitric acid/nitric oxides) stored at the Mingechevir depot does not pose an immediate hazard, even though most tanks already show leaks and larger spills occur from time to time. Except personal protection equipment, the necessary equipment for emergency response in case of spills is still available, namely pumps, 10 cubic metres of ammonia as a neutralizing agent and backup tanks. However, continuous leakage of smaller quantities of oxidizers is obvious and the storage can not be regarded as safe.

Large quantities of isopropyl nitrate that are stored in sheds separated from Samine and oxidizers by a distance of 50 metres and 150 metres respectively pose a larger threat. A strong, isopropyl alcohol-like smell inside and outside the sheds indicates that at least some of the barrels lying and standing in the sheds are leaking. As isopropyl nitrate is highly flammable, explosive and Location of Missile Fuel Component Storage Sites and Risks

forms explosive vapours in ambient air, acute danger of explosion has to be assumed for the isopropyl nitrate storage sheds. As the quantity of isopropyl nitrate stored in the sheds sums up to approximately 24 metric tons, an accident would also affect the storage facilities for Samine, oxidizer and conventional fuels (diesel, kerosene, gasoline, etc.), thus resulting in a major catastrophe that would also effect the local population in surrounding villages.

# 5. **RECOMMENDATIONS**

In order to prevent major accidents or spills resulting in the loss of human life or health of the civil population in the areas surrounding the depots at Alyat and Mingechevir; and in accordance with the risk assessment described above, the following immediate measures should be implemented as soon as possible:

- 1. Provide ammonia solution as a neutralizing agent, in particular for the Alyat depot
- 2. Provide appropriate pumps and pipes to the depots for both oxidizer and Samine pumping in case of emergency
- 3. Provide ten personal protection equipment sets for both depots

With respect to the storage situation of Samine and isopropyl nitrate at the Mingechevir depot, immediate action including the recovery of Samine and TM-185 from tanks in contact with groundwater and the destruction of isopropyl nitrate as soon as possible is recommended.

The measures recommended here are independent from any final solution with respect to the destruction or utilization of Melanj, Samine and Isonite. The only concern of these recommendation is to improve the safety of the storage until a final solution is implemented.

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# 7. PHOTO DOCUMENTATION

*Photograph 1*, Leaking oxidizer tank. With a close-up it becomes clear that the safety valves have corroded away due to contact with concentrated nitric acid. They were found lying on the ground near the tank.



*Photograph 2.* This oxidizer tank at the Alyat Depot is lying on the bare ground. Due to corrosion and rocks penetrating the tank hull, a large spill with the loss of all oxidizer from the tank occurred recently.



*Photograph 3*, Detail of another oxidizer storage tank at the Alyat depot that has been leaking recently.



*Photograph 4*, Mechanism used to pump Samine at the Alyat depot. The pump is no longer functioning and can probably not be repaired. A replacement pump would be necessary.



#### Location of Missile Fuel Component Storage Sites and Risks

*Photograph 5*, Storage of Samine rocket fuel in tanks similar to those used for the storage of the oxidizer at the Alyat depot. The tanks are lying on the bare ground. A strong characteristic amine odour surrounds the storage site.



Photograph 6, Close-up of a Samine storage tank at the Alyat depot.



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*Photograph 7*, Close-up of oxidizer storage tank caps at the Mingechevir depot. As in Alyat, safety valves have corroded away and are lying on the ground. Nitrous gases escape continuously.



*Photograph*  $\delta$ , Close-up of a large leak at the top/cap of an oxidizer storage tank at the Mingechevir depot. The tank is now empty.



#### Location of Missile Fuel Component Storage Sites and Risks

*Photograph 9,* Storage of Samine and TM-185 in 50 cubic meter tanks in a pit at Mingechevir. Due to the high groundwater table, the tanks have been in contact with groundwater for more than ten years. A strong characteristic Samine and kerosene/gasoline odor was observed. The groundwater table seems to be varying, speeding up corrosion of the steel tanks due to contact of wet surfaces with oxygen.



*Photograph 10*, Close-up of a Samine tank in contact with groundwater in a pit at the Mingechevir depot.



*Photograph 11*, Dark-red to violet colour of the soil surrounding the pit with Samine storage tanks at the Alyat depot. The colour is probably due to a reaction of triethylamine cations with soil compounds. The contamination extends over an area of at least one hectare.



# DISPOSAL OF ROCKET FUELS STORED AT ALYAT AND MINGECHEVIR DEPOTS, AZERBAIJAN

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Abstract An Engineering Process for treatment of rocket fuels and oxidizers is developed. This process includes establishing design criteria, selecting alternatives for each waste stream, and evaluating each alternative versus each criteria for the design. Recommendations re presented for each of the five waste streams.

Keywords: Samine; melanj; neutralization Isonite; Alyat; Mingevecir

#### **1. INTRODUCTION**

The details of the hazards posed by the chemicals being stored at Alyat and Mingechevir has been well described by Dr. Mamedov of the Azerbaijan National Academy of Sciences and Professor Dr. Spyra of Brandenburg University of Technology at Cottbus. From this evidence, it is clear that removal and disposal of these chemicals is justified. The goal must be the safe treatment and disposal of the chemicals, safe removal and disposal of any hazardous soil residues, and the decontamination and recycle of the metals in the storage containers. The chemicals to be disposed of are shown in Table 1, along with data that define their chemical properties and significant health risks. Following well established standards for cleanup of hazardous and toxic waste (LaGrega 1994), the design process should consist of the following steps:

- 1. Establishing objectives or design criteria; developing alternatives for each waste stream
- 2. Evaluating each alternative based on effectiveness, reliability, implementability, and costs; and

3. Selecting a design based on weighted analysis of the design criteria (King 1996).

In regard to the design process, the waste streams that should be separately evaluated are:

- 1. The oxidizers AK-20k, AK-27p, and AK-27i: Each composed of different amounts of nitric acid and nitric oxides
- 2. Samine: A combination of equal volumes of triethylamine and xylidine
- 3. Isonite: Isopropyl nitrate
- 4. TM-185 20% Gasoline and 80% kerosene
- 5. Metal tanks, fixture, and piping

Chemical type/ Property	Oxidizer: nitric acid -HNO <sub>3</sub> ,	Oxidizer: nitric tetroxide-N <sub>2</sub> O <sub>4</sub>	
Amount:			
Kilograms	1,000,000	400,000	
Liters	677,000	241,000	
Molecular weight	63	92	
Physical description	Colorless to yellow liquid, suffocating odor	Yellow-brown liquid, acrid odor	
IDHL	100 ppm	50	
Worker exposure limit	2 ppm	1 ppm	
Hazards	Heat in combination with water, corrosive, acid burns	Flammable, toxic	
Volume ratio, ppm to mg/m <sup>3</sup>	1 ppm = 2.62	1 ppm = 1.91	
Incompatible chemicals	Combustibles, metal powders	Ammonia, water, oil	

Table 1a, Data on Chemicals to be disposed of from Alyat and Mingechevir (Oxidizers)

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Chemical type/			Izonite,	TM 185
Property	Triethylamine	Xylidine	isopropyl nitrate – C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	kerosene and gasoline
Amount:				
Kilograms	225,000	225,000	24,000	
Liters	310,000	229,000	22,400	
Molecular weight	101	121	105	
Physical description	Colorless liquid, ammonia odor	Pale yellow liquid, amine odor	Colorless liquid	
IDHL	1000 ppm	150	2000	
Worker exposure limit	10 ppm	2	25	
Hazards	Flammable, toxic	Flammable toxic	Flammable, toxic	Flammable
Volume ratio, ppm to mg/m <sup>3</sup>	1 ppm= 4.21	1 ppm = 5.04	1 ppm = 4.37	
Incompatible chemicals	Strong oxidizers	Strong oxidizers	Strong oxidizers, combustibles	flame

*Table 1b,* Data on Chemicals to be disposed of from Alyat and Mingechevir (Fuels)

# 2. DESIGN CRITERIA OF THE TREATMENT AND DISPOSAL

The first task in developing and evaluating methods for disposal of the hazardous materials just listed is to establish a set of design criteria. Foremost in designing the final treatment and disposal plan is assuring the maximum safety short and long-term. This first requires protecting the health of the public who could be exposed to releases of these chemicals. A second health concern is for the safety of the workers who will conduct the disposal operations. These chemicals are extremely corrosive, volatile and toxic when released to the air, soluble and toxic in water, can be ignitable or explosive if not properly handled, and can generate high temperatures spontaneously. Overall, these are an extremely hazardous collection of chemicals!

A second concern that will affect the design is the evidence that shows that the chemicals are in a degraded state after years of open storage. Storage tanks are rusted and leaking, which makes handling difficult and dangerous. These liquids tend to become more viscous with age, thus more difficult to pump and move. Oxidized metals and other corrosion byproducts dissolved in the fluids change the chemistry of the expected reactions and can create

unexpected solid residues. Degradation byproducts from some of these chemicals can produce toxic gases that will be released upon opening of the tanks and these pose an immediate safety hazard to workers. And finally, all of these factors contribute to the tanks being very difficult to completely empty and to clean to safe standards before the metals can be recycled.

There is also strong evidence that materials have leaked from some tanks. These spill residues can pose a health risk to the public, if they contaminate the groundwater. Highly contaminated soils must be considered in addressing remedies selected for the site. Treatment options that can handle both the pure chemicals and contaminated soils would be preferred.

With this as a general overview of the design process, the following criteria are proposed for the remediation design:

- 1. Protecting the public health is the most important criteria. Short –term, the concern is with control of the release of toxic chemicals, the concern for fires and explosions, and spill prevention and containment.
- 2. Worker safety must be heavily considered in the design. Many hazards exist in the handling and treatment of these chemicals, all of these must be accounted for in the design.
- 3. Treatment methods should produce non-toxic residues, with a goal that materials have a secondary use such as land application for agriculture or recycling into industrial uses.
- 4. On-site treatment will be the preferred option to reduce the risk of exposure during transport of materials.
- 5. Cost will be a basis for selection once health risk standards are met.
- 6. Use of local resources and capabilities is preferred. These criteria would infer that simple solutions such as neutralization and thermal destruction would be preferred if the required treatment standards can be met. Where this is not practical, disposal and treatment facilities closest to the two sites will be preferred.
- 7. System should be designed assuming it will be used for these two sites only. This reinforces the idea that simple designs are preferred because their will be no continued value of whatever system is built.

## 3. DEVELOPMENT OF ALTERNATIVES

In general, the cleanup process must address treatment options for each of the five waste streams listed in Paragraph 1. a.- e., on an individual basis. A consideration to be made is whether to build treatment facilities at each depot

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or to build one treatment system at either Mingechevir or Alyat with the chemicals at the other facility being transferred to the treatment site. Both of these options need to be part of the alternatives considered. The discussion of the alternatives will be developed on the basis of treating each waste stream, which will be followed by considering the locations for treatment.

## 3.1 Oxidizer Treatment Alternatives

The oxidizers are three different concentrations of nitric acid and nitric oxides with small concentrations of iodine or fluorine. The ratio of nitric acid to nitric oxide (73 to 80 percent) is not critical in designing a method of treatment and disposal. Considering the age and storage conditions of the chemicals, it should be assumed that other impurities have contaminated the solution. Options available are:

- 1. Commercial resale to a process that needs a strong acid/oxidizing agent.
- 2. Chemical reaction with ammonia to form fertilizer.
- 3. Chemical neutralization to form salts that can be safely released to the environment.

#### 3.1.1 Option 1

It must be assumed that all of the material would have to be moved to different containers for shipping and that all metal tanks would have to be cleaned for resale or scrap metal recycling. There is no simple method to separate the two primary chemicals (HNO<sub>3</sub> and  $N_2O_4$ ) or to remove the iodine or fluorine; therefore, any reuse must be tolerant of these limitations. The total volume of this material is just over 900 cubic meters, in two locations, widely separated. Based on all of the conditions just described, the resale for commercial use would seem unlikely. Further, the hazards of transport, handling for repackaging, and possibility of spills and releases of concentrated oxidizers does not meet several of our design criteria.

#### 3.1.2 **Option 2**

The benefit of this option is producing a valuable commercial product, ammonium nitrate fertilizer. The chemistry of making ammonium nitrate from nitric acid and ammonia is straightforward. However, how this reaction proceeds with nitric tetroxide present is not well understood. In the presence of warm water:

$$N_2O_4 \rightarrow 2 NO_2$$
 (1)

and then

$$2NO_2 + H_2O \rightarrow 2HNO_3 + NO$$
 (2)

It can be expected that a reactor could be designed to achieve some reaction of ammonia and nitric tetroxide, but the chemistry is more complex. Further, the release of toxic gases and worker hazards are significant in this process. Handling up to 1 million liters of ammonia creates another hazard for operations. Finally, ammonia nitrate is an explosive hazard and thermally unstable (Bailer 1965), both of which increase the risk to public health and safety.

#### 3.1.3 Option 3

This option is the most scientifically simple solution to the problem, though several options for neutralizing agents are available. The chemical bases that can be considered are those that are most likely to be available, including strong bases such as sodium hydroxide, and common natural minerals such as calcium carbonate and lime. The chemistry of neutralization is simple and well known for both nitric acid and nitric tetroxide, as seen in the example below for lime:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
 (3)

$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$$
(4)

Noting reactions (1) and (2) above, nitric tetroxide would also be neutralized with lime. Fluorine and iodine would be chemically bound in these reactions, mostly likely in a metals complex with nitrate. In all neutralization reactions with concentrated acids, heat generation is a concern. Dilute solutions should be produced before the neutralizing reactions to reduce hazards to the public and to workers. Lime or calcium carbonate are cheap, available, and can be safely handled and shipped so they do not increase the risk to the public or to workers. Use of strong bases would increase worker exposure to hazardous chemicals and represent a public hazard in shipping and storage. Dilute solutions of calcium nitrate could be land applied as a soil conditioner for its nitrate value. This solution should be applied with care so that nitrate levels

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in the groundwater are not increased. Simple reactors fabricated on-site would be acceptable for this process and local workers could handle the operation of the process. Overall, this process best meets the design criteria presented above for detoxifying the oxidizers.

## **3.2** Treatment Alternatives for Samine

This chemical consists of equal amounts of triethylamine and xylidine, both combustible liquids. One third of the material is stored at Alyat and two thirds is located at Mingechevir. The hazards posed by these chemicals include worker exposure to low concentrations of vapors of xylidine, explosions if samine is mixed with incompatible chemicals (acids or oxidizers), and fire if ignited. Options available for managing these chemicals include: 1) distillation and separation of the chemicals for resale, 2) combustion for energy recovery, and 3) incineration for disposal.

#### 3.2.1 Option 1

Distillation is a practical means of managing this waste only if the resale value of the recovered material is sufficient to defray the cost of the distillation operation. Xylidine is expensive in reagent grade formula, as much as \$US 100 per liter, while triethylamine in the reagent grade costs about \$US 100 for 4 liters. Because of contamination with corrosion by-products and other contaminants, it would be expected that the xylidine and triethylamine recovered from this process would be worth only a small fraction of these amounts. Further, distillation to this level of purity would require very expensive treatment. No bulk prices for these chemicals could be accurately obtained. The only practical means would be a portable unit that could be moved to both sites. Building and operating a distillation device just for this waste would not be practical. This activity would necessarily require a contract for complete processing of the samine by a private firm. Once separated the material would have to be repackaged and shipped to a buyer.

#### 3.2.2 **Option 2**

Because of the high energy value of these materials, they could be used as a fuel in certain types of combustion systems. They should not be introduced directly, but would have to be mixed with other liquid fuels in small concentrations. Combustion products would be carbon dioxide, oxides of nitrogen and water; the concentrations of theses gases would not be greatly increased over burning of fossil fuels such as oil. This option is keyed to finding an existing combustion process, a cement kiln as just one example,

that is located within a reasonable distance and that can be reached without exposing a large population during transportation. Systems to mix the waste with fuel or to slowly inject the liquids are readily available commercially. It is expected that these materials would have little resale value as a fuel because the quantities are small and this is a one time application.

#### 3.2.3 Option 3

There is the option to incinerate the materials to reduce the toxicity without energy recovery. Portable incinerators are commercially available that could be brought on-site at each depot to burn these materials. This would be costly and could not be accomplished using local resources. This option seems least favorable in comparison to the established design parameters.

## 3.3 Isonite

This material is a flammable liquid that is less toxic or hazardous than either xylidine or triethylamine. Isonite can be treated by either combustion or incineration in the same process as the other two chemicals. Distillation could be used to purify Isonite if commercial resale were economically feasible.

#### 3.4 TM 185

This is a fuel that may be mixed with fuel oil and burned in any standard boiler or combustion system.

## 3.5 Metals

Processing of the tanks and the associated valves and fixtures must be accomplished as part of the overall process design. Foremost, any design must assure that all hazardous residues are safely removed from the tanks before they are released to other uses. All tanks must be drained and cleaned. If practical, the residue from cleaning the tanks should be processed through the same system that is designed for treatment of the primary waste materials. For example, if neutralization is used for treatment of the oxidizers, the wash water from the tanks could be used in the neutralization tanks to dilute the acids. This option can be conducted on-site or could be completed at a local facility that has the capability to decontaminate and reprocess the metals.

Some of the tanks may be suitable to build the reactors within the neutralization process. Valves and piping will need to be drained and

#### Disposal of Rocket Fuels at Alyat and Mingechevir Depots

decontaminated. This will require special care because sludges and viscous materials tend to be trapped in these devices. Another note of caution concerns entry into the confined space of the tanks with samine and Isonite. Even small residues of these chemicals in the tanks can yield deadly levels of vapors inside these tanks as these vapors are heavier than air and will collect inside.

Metals processing can be accomplished by with resources within the area of the depots. Specific protocols will need to be developed for safety procedures and the appropriate safety equipment will be needed for the workers.

#### 4. ANALYSIS OF ALTERNATIVES

A complete analysis of alternatives is a product of the workshop meeting conducted at the end of November in Baku. There are questions and data that needed to be addressed by local experts before this analysis could be completed. Table 2 presents a framework and a preliminary attempt at this analysis, which is offered as a starting point for the groups deliberations.

	, Alternatives	Public	Worker	Toxicity	On-site	Cost	Using
		Health	safety	of waste	Treatment		local
				products			resources
Waste/	Alternative			_			
Oxidiz	ers						
- Res	ale	А	В	В	NA	U	F
	monia	В	В	F	А	М	F
- Neu	tralization	А	А	А	А	L	Α
G .							
Samine		D	D	D		TT	Г
	tillation	B	B	B	A	U	F
	nbustion	A	A	A	B	L	A
- Inc	ineration	A	A	A	В	M/H	A
Isonite							
	nbustion	A	A	А	В	L	A
- Inc	ineration	А	А	А	В	M/H	А
TM 18	5						
	nbustion	А	А	А	В	L	А
Metal			D	D		T	
- On-	-site decon	A	В	B	A	L	A
	Off-site	A	A	В	F	M	F
recycle	2						<u> </u>
	Codes			Cost codes			
	A – Acceptable B – Marginal or uncertain F – Fails to meet criteria			L – low cost M- medium cost			
				H – high	ii cost		
				3			

U-uncertain

Table 2, Alternatives Analysis for Treatment and Disposal

NA - Not applicable

#### 5. **RECOMMENDATIONS**

The following recommendations are made as a way to generate discussion that will lead to the group reaching final recommendations concerning this project.

- a. Public health is the most important consideration in the cleanup design.
- b. Worker safety is very important to success in this project.
- c. Some form of chemical neutralization is the safest and simplest process for treatment of the oxidizers.
- d. Combustion for energy recovery is the best method of disposal of the samine and the Isonite. This alternative requires finding a suitable existing facility capable of burning these wastes as a supplemental fuel.
- e. Distillation is viable for samine only if a market for the products can be found that makes this a cost effective solution.
- f. TM-185 should be burned as supplemental fuel in an oil boiler.
- g. Metal parts, once decontaminated, can be resold for reuse or as scrap metals, depending on the condition of the tanks and fixtures.

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# PAST EXPERIENCE IN THE TREATMENT OF ROCKET FUEL COMPONENTS AND THEIR INDUSTRIAL FLOWS

Koray Balkaya, Alexander Medvedsky, Alexander Emelyanov *MD Industries Ltd:, Turkey and Stroom RITIE, Ukraine* 

Abstract The Ukrainian firm Stroom has been working for more than five years on the neutralization and destruction of liquid rocket fuels. It has worked on projects with the United States Department of Defense as well as completing projects in Russia and Moldova. This report describes Stroom's successful destruction of the Moldavian stock piles of melanj and samine and suggests applications for the situation in Azerbaijan.

## **1. INTRODUCTION**

The participation in demilitarization projects is one of the main activity directions of Stroom Research Innovative Technology Implementation Enterprise (Ukraine, Vinnitsa). These projects are mainly aimed at the elimination of rocket fuel components, toxic and hazardous substances.

For more than 5 years the enterprise has successfully performed the work on the liquid rocket fuels neutralization, incineration and processing, utilizing its own technologies.

To perform these projects the enterprise possesses a well-developed production base, complex of special aggregates and equipment, highlyqualified personnel with vast past experience in rocket fuel components treatment, and necessary licenses for this work performance.

## 2. SIMILAR WORK PERFORMANCE IN PAST EXPERIENCE

During 1998 Stroom performed several contracts for US DOD Defense Threat Reduction Agency to develop technologies and perform work related to the elimination of hazardous and toxic waste:

- 1. Elimination of ground water contamination with toxic substances (heptyl industrial liquids).
- 2. Upgrade and modernization of regular incinerators to increase their efficiency and concentration of rocket fuel components industrial flows under the incineration.

The developed technologies and cooperation that had been established among some specialized institutions in Ukraine and Russia allowed the performance of a number of projects in 1999-2000. These projects included the neutralization and disassembly of the equipment at two Unified Fuel Facilities (UFF) of ICBMs in Khmelnitsky and Pervomaysk (Ukraine).

To ensure the work special technologies were developed to de-contaminate the equipment, soil, buildings and structures that had contacted liquid heptyl and amyl for a long time.

In total more than 23 km of pipe-lines, 58 reservoirs from 2 to 125 cubic meter capacity, about twenty buildings and structures were neutralized and dismantled.

In 2002 Stroom together with foreign partners performed the contract with NAMSA for the elimination of about 350 tons of melanj (rocket fuel oxidizer) and neutralization of fuel tanks in 11 SA-5 "surface-to-air" missiles in the Republic of Moldova.

# 3. HIGH TEMPERATURE ELIMINATION TECHNOLOGY

Stroom has developed the technology of the high temperature decomposition (incineration) of melanj industrial liquids (30-50% concentration in cyclone ovens, installed at special aggregates). This technology also allows the current and further equipment neutralization.

Past Experience in the Treatment of Rocket Fuel Components

The utilization of this method for the elimination of toxic substances and rocket fuel components has some economic and ecological advantages:

- High mobility of aggregates which allows the work to be performed immediately at the storage sites
- Rocket fuel is used as the power source while it is being eliminated
- The incineration is being performed under low (up to 3-5%) consumption of other fuels
- The elimination of rocket fuels (exhausts concentration) is in the full compliance with modern environmental requirements
- Expenses are optimized on the account of reliable and certified aggregates, even under the condition that they have to be upgraded to burn samine and isopropyl nitrate fuels
- There is no need in the development of high-cost technologies

This technology at the same time has some disadvantages:

- High power consumption
- Relatively high need in diesel fuel
- High corrosion while contacting low concentration rocket fuel components industrial flows.

This technology was used for the elimination of melanj in the Republic of Moldova.

## 4. **NEW TECHNOLOGIES**

At present time the experts of the enterprise have developed new technologies which include the de-contamination of melanj by their chemical treatment utilizing special agents – widely spread substances, raw materials, including those of industrial waste. The final product is in a granule state.

The chemical de-contamination technology consists of the melanj and special agent mixture through which melanj is completely neutralized. The final products are useful chemicals that may be used for the production of mineral fertilizers.

The ecological value of the melanj chemical de-contamination lies in the fact that it is possible to get non-toxic substances. Secondary waste are absent and do not require additional treatment or burial. The hazardous impact on soil, ground water is excluded.

This technology has the following advantages:

- Lower cost in comparison with the incineration
- The technology is environmentally safe
- Ability to perform the de-contamination immediately at fuel storage sites
- The final product may be used for the production of mineral fertilizers

## 5. DECONTAMINATION OF ROCKET FUEL COMPONENTS

The de-contamination of rocket fuel oxidizers (melanj) may be performed by both of the technologies listed above.

The de-contamination of Samine and isopropyl nitrate fuels is performed by their incineration in the special aggregates. This process also insures emission of the admittedly hazardous substances into the air.

## 6. CONCLUSIONS

The technology of the incineration that has been applied in Moldova proved to be the only suitable technology due to the following reasons:

- Because of the urgent need of elimination of toxic substances that might cause a serious environmental disaster
- Absence of transportation possibilities of melanj anywhere outside Moldova;
- Absence of any industrial or other local capacities for melanj treatment
- No need for the final product of melanj treatment on the part of Moldova

As for Azerbaijan the most reasonable way seems to be in the combination of several technologies that prove to be the most efficient from the point of view of the environmental and social security and cost-effectiveness.

The incineration may be necessary in treating leakage, contaminated soil and residuals of industrial flows in the tanks and pipe-lines and vapors.

# TRANSFORMING LIQUID ROCKET FUEL COMPONENTS INTO USEFUL PRODUCTS: EXPERIENCE IN GEORGIA

#### Prof. Dr. Avtandil Dolidze

P. Melikishvili Institute of Physical and Organic Chemistry of the Georgian Academy of Sciences; The Military-Technical Engineering Academy of Georgia

Abstract This case study recounts the successful destruction of melanj and samine stockpiles in the Republic of Georgia. This project was supported by the Organization for Security and Co-Operation in Europe. A method of neutralization developed by Avtandil Dolidze was able to create a biproduct which could safely be used as agricultural fertilizer to grow corn on Georgian soils.

#### **1. INTRODUCTION**

After the withdrawal of the Soviet/Russian Military Forces from Georgia, a large amount (about 1000 tons) of poisonous Rocket fuel liquid components were left behind in the area of the former military bases in Soganlugi (near Tbilisi, capital of Georgia), Chaladidi and Meria (near the Black Sea). That batch of components of liquid rocket fuel was brought to Georgia in 1988.

P. Melikishvili Institute of Physical and Organic Chemistry was assigned as a provider of works on utilization of liquid rocket fuel components by the presidential decree no. 401 of August 28, 1997. I was assigned as a coordinator of these works.

Fuel samine TG-02 is a mixture of triethylamines and isomeric xylidines (1:1). This product was elaborated in Germany under title "Tonka-250". Oxidizer melanj AK-20k contains (in mass. %): nitric acid – 73; nitrogen oxides ~ 22; HF ~ 0,5; H3PO3 – 1,3; water – 2,5; etc. This product was elaborated in US for rocket system "Nike-1". Anticorrosive additives were elaborated by the Californian Technological Institute.

According to the Soviet Army instructions samine should be neutralized by boric acid solution later mixed with kerosene and burned in open furnaces. Melanj used to be neutralized by causticum sodium solution and later the obtained aqua-soluble salts liquidated.

#### 2. DESTRUCTION OF SAMINE

Naturally, we couldn't just burn the mixture of samine and kerosene outdoors within the city boundaries or subtropics zone near the Black Sea.

Social factors have an important role in this kind of work. The local population is very suspicious about these activities and demands detailed information. I met the representatives of local population and different political organizations trying to explain them the situation.

Thus during the winter period of 1998-1999 we organized fractional distillation of samine on the territory of the Institute. Handmade distillation apparatus from 200-liter iron tanks were used. Three fractions were separated: (a) up to 110°C consisting mostly of triethylamine, (b) transition fraction and (c) fraction of isomeric xylidines at 190-225°C. The transition fraction made only several percent of initial capacity. Fractions of triethylamines and isomeric xylidines were distillated in practically equal quantities.

The noted examples of samine fractional distillation were tested in Lab conditions but it was necessary to perform high tonnage test as well. According to the conclusion of the Georgian Institute of Plant Protection the triethylamine fraction could be used as contact herbicide. Treatment of most polluted parts of railroad net by triethylamine was performed in less populated places using special railway carriage – a herbicide splashier. Thus the triethylamine fraction became useful, as well.

Antidetonating compositions based on isomeric xylidines with octane number 106 were also prepared. Georgian crude oil has a paraphine-naftenic nature and after direct distillation the petrol fraction (so called nafta) has a low octane number. Addition of 2-3 vol. % of antidetonating compositions, based on xylidines increases the octane number. Thus, the greatest part of processed samine was used for increasing the octane number of low-octant petrol.

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## 3. DESTRUCTION OF MELANJ

First of all, the total amount of melanj was offered to the Rustavi Chemical Plant AZOT. Amonium Celitra is produced from nitric acid (concentration 58 %) and it costs 4-5 cents per kg. On the other hand, preparation of melanj for transportation in special volumes, transportation, unloading and conditioning using the plant technology increases production cost to 22 cents per kg. Naturally, the plant was categorically against this "gift" because its amount was too small for the plant (it would be used-up within a few hours or days) and would not compensate the applied expenses.

That is why we worked out a new melanj utilization scheme. Diluted melanj was neutralized by aqueous solution of slack lime and as a result so called Norwegian celitra was obtained. Diluted Norwegian celitra was used as fertilizer for local soils.

The first half, 2002 Organization for Security and Co-Operation in Europe (OSCE) funded Project of melanj Neutralization in Meria, Ozurgeti District (about 450 tons). Prof. A. Dolidze was entrusted with implementation of the OSCE Project melanj based on the Georgian proposal. A group of German experts undertook technical inspection and together with the OSCE Mission to Georgia, controlled over the completion of scheduled works. During the final visit the Expert Group made sure that the OSCE Project was successfully completed. They concluded that:

The poisonous and environmentally harmful liquid missile fuel melanj was fully utilized.

The missile fuel neutralized with slack lime was thus turned into a harmless and agriculturally useful nitrogen fertilizer.

No accident was recorded during the whole period of works.

The budget allocated by the OSCE was sufficient and allowed to carry out necessary works on time.

## 4. CONCLUSIONS

This method tailored for local conditions may be considered as utilization technology for remaining liquid missile fuel in similar storage facilities or on missile bases.

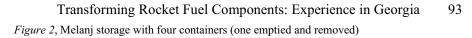
Photos taken during the Melanj Project implementation are shown on figures 1-11.

After the project finalization a special act about obtained results was jointly issued by local ecological service, local government representative, the territory owner and the project supervisor.

Due to the fact that ecological stability of the environment is a critical part of the social stability of the population, this becomes extremely important. Therefore, the conduction of the rehabilitation activities stated in the project is considered as a one of the main leverages for the stability in the region.

Figure 1, Impressions from the first visit-four years of storage without control





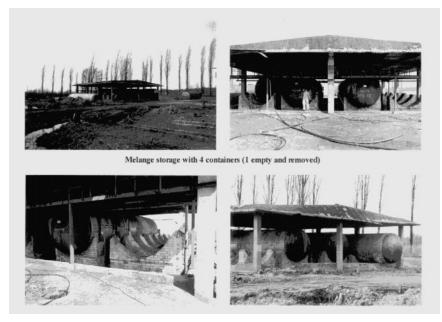


Figure 3, Container for mixing oxidizers and neutralization of nitric gas (little container)



Container for mixing oxidizer and neutralization of nitric gas (little container)



94 NATO Advanced Research Workshop in Azerbaijan Figure 4, Production of neutralization liquid "Lime Milk"



Production of neutralization liquid "Lime milk"



Figure 5, Open containers with acid-resistant pipelines



Open containers with acid-resistant pipelines



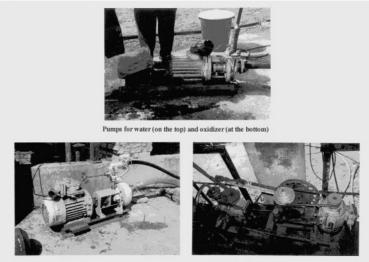


Figure 6, Pumps for water (top) and oxidizer (bottom)

Figure 7, Complete protective clothing for the staff

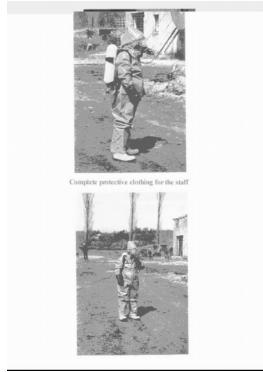


Figure 8, Former samine storage-containers removed

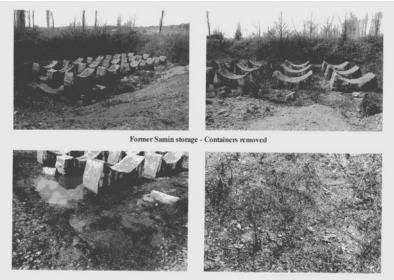
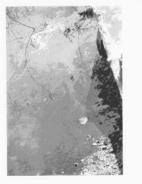
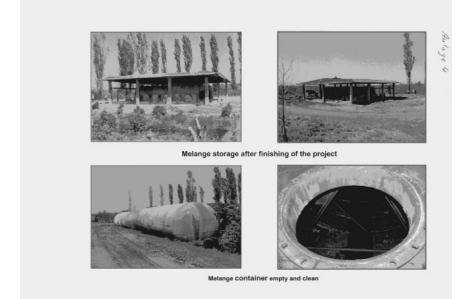


Figure 9, With samine polluted surface area of former samine storage

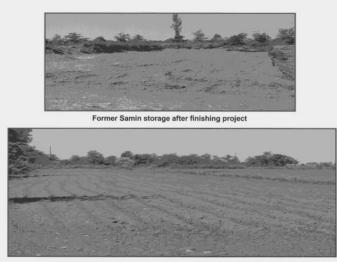


With "Samin" pollutes surface area of former Samin storage





*Figure 11*, Former samine storage after finishing project (top). Green fields with help from fertilizers of mélange neutralization (bottom)



Green fields with help from fertilizer of Melange neutralization

## SUPPORT TO PARTNERSHIP FOR PEACE TRUST FUND PROJECTS BY THE NATO MAINTENANCE AND SUPPLY AGENCY (NAMSA) THE PROJECT IN MOLDOVA TO DESTROY MELANJ ROCKET FUEL OXIDISER

Steve Brown

Senior Technical Advisor Partnership for Peace Projects Group—Ammunitions Sector NATO Maintenance and Supply Agency

Abstract The destruction of the Moldavian stockpiles of malanj was completed in 2002 through a NAMSA project with the Netherlands as the lead nation. Private firms were invited to apply to carry out the melanj disposal and in the end the Brittish firm John Brown was awarded the contract. This report describes the practical aspects of this melanj disposal and how it was finally completed.

## 1. GENERAL

In February 2001, The Netherlands Delegation at NATO Headquarters tasked NAMSA to produce a project proposal for the destruction of hazardous rocket propellant oxidizer and surplus munitions in Moldova. The Netherlands as the Lead Nation of the project subsequently accepted NAMSA's proposal for a project lasting 14 months at a total cost of USD 1,079,000. The other contributing countries were Canada, Germany, Hungary, Luxembourg, Poland, the United Kingdom and the United States.

More than 300 tonnes of the rocket propellant oxidizer (known as melanj) were contained in leaking storage tanks and in the fuel tanks of guided missiles at a military site close to the capital, Chisinau. An international consortium headed by the British company John Brown Engineering won a contract to dispose of the Melanj and clean up the site.

The task was completed by a process of incineration in specially adapted mobile units imported from Ukraine between May and October 2002. The Ministry of the Environment and local environmental groups monitored the process closely. There were no safety or environmental problems.

The project started on 1 November 2001, with NAMSA acting as the executing agency. It was managed by NAMSA's project management, contracting and finance staff in Luxembourg assisted by an in-country team of two locally employed personnel working from an office in the Moldovan Ministry of Defence.

#### 2. IMPLEMENTATION OF MELANJ DISPOSAL PROJECT

Implementation of the project depended on the signing of a number of agreements, as follows:

- NAMSA-Moldova Memorandum of Understanding: This was finalised in June 2001.
- Executing Agent Agreement: NAMSA and The Netherlands Delegation to NATO signed an Executing Agent Agreement to define the terms of their cooperation for the execution of this project.
- Financial Management Agreement: This agreement between the Financial Controller at NATO Headquarters and the donors had to be complete before NAMSA could start the project.

#### 2.1 Project Start-up

The project could only start after all the agreements listed above had been finalized. The start date was 1 November 2002. The first requirement was the signing of a Cooperation Agreement between NAMSA and the Ministry of Defence and the recruitment of the in-country team. NAMSA accomplished this during a visit to Moldova on 7-10 November 2001.

#### 2.2 Formulation of RFP

Developing a Request for Proposals (RFP) including a detailed Statement of Work for the destruction of the melanj was a high priority. Work started on this before the official start date of the project. The Statement of Work detailed the required outputs and specified the environmental and other limitations but did not specify how the contractor should do the work. The RFP was issued to 8 selected industrial sources in November 2001 with a The NATO PfP NAMSA Project to Destroy Melanj in Moldova 101 closing date for the submission of bids of 28 February 2002. The RFP invited potential bidders to attend an on-site Bidders'

Conference in Moldova on 14-15 January 2002 and stipulated that bids would be accepted only from companies that were represented at the conference.

## 2.3 Bidders' Conference

Representatives of three potential bidders, the German companies Nammo-Buck and EBV, and a consortium headed by John Brown Engineering (UK) attended. The conference was held in two parts; a visit to the melanj storage site at Dançeny on Monday 14 January followed by a formal meeting between the potential bidders, NAMSA and a technical advisory team from the MOD.

After some opening remarks from the NAMSA team concerning the mechanics of responding to the formal Request for Proposals (RFP) the main activity of the conference was in the form of a question and answer session with the NAMSA and MOD representatives dealing with pre-presented written questions and others posed by the bidders covering technical, operational and contractual issues.

## 2.4 Award of Contract

Two bids were received by NAMSA by the competition closing date; from NAMMO Buck and John Brown (UK). After scrutiny of the technical content of the bids and responses to supplementary questions from NAMSA to the bidders the contract was awarded early in May 2001 to the consortium headed by John Brown (UK), which included the US company ATK Thiokol and the Ukrainian company Stroom. These companies had acquired considerable experience over the previous ten years in the disposal of rocket fuels and oxidizers throughout the former Soviet Union, although they had not previously tackled melanj. The price quoted was within the project budget.

Their proposal was to deploy from Ukraine mobile cleaning, neutralizing and incineration equipment. All neutralization and disposal action would take place on the site, thereby avoiding the inherent dangers of transporting these toxic and volatile materials over public road or rail links. John Brown's plan foresaw completion of the disposal program well before the onset of winter.

The NAMMO Buck proposal required transportation of the melanj by road to a permanent facility in Germany. This was rejected because the contractor was unable to confirm that approvals to transport this hazardous material

through Hungary and Austria, the proposed route, and the proposal was conditional on obtaining that certification.

#### 2.5 Importation of Equipment

The first 6 weeks of the contract period were spent by the contractor in securing the necessary export and import documentation from the Ukraine and Moldova authorities, and in preparing the equipment and moving it to the Ukraine-Moldova border. Although the equipment was now owned by a civilian company and was used for peaceful purposes, it retained its military character and it was therefore classed as dual purpose. For this reason, special authorization was necessary from the defence ministries of Ukraine to export it and Moldova to import it, as well as from the Ukraine Export Department and Moldova Customs Department. The NAMSA Representative played a key role as liaison between the contractor and the Moldovan authorities during this period.

#### 2.6 **Operational Phase**

With the necessary authorisations secured, the equipment moved on site on 25 June 2002 and, following a period of commissioning and testing, incineration operations began on 9 July 2002. Detailed trials enabled the contractor to incinerate a 30% melanj solution with no increase in polluting environmental emissions. As the project progressed, this was gradually increased to a 40% solution with no adverse environmental effects. This enabled a more rapid incineration program to be undertaken with savings in time against the original schedule.

The contractor and the Moldovan Ministry of the Environment undertook regular monitoring of the incineration, which confirmed that emissions were well within acceptable limits.

In parallel to these operations other tasks started including decanting of samine and melanj from SA-5 missiles, the preparation of storage tanks, cleaning and neutralising existing tanks and other support functions.

Within a few weeks of the start of operations, more than 40 people were employed on the task; including 20 locally employed Moldovan staff.

Incineration of the original quantity of Melanj, 325 tonnes, was completed on 4 October, ten days ahead of schedule. Final decontamination of on-site

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equipment and surface clean up around the storage site was completed by 11 October. However the contractor agreed to retain men and equipment on site for a limited period pending a decision from the Lead Nation to provide funds for additional work that had been requested by the Moldovan MOD.

## 2.7 Additional Tasking

The Moldovan Ministry of Defence requested additional work to drain the melanj tanks of 3 SA-5 missiles they had discovered in addition to the 8 that had been included in the contract. They also requested the incineration of bulk stocks of samine rocket fuel. The samine request was rejected by NAMSA because it fell outside the terms of reference of the project and it would have been an expensive operation. However the project would have been unfinished if any melanj stocks had been left at Danceny, so NAMSA requested funds from The Netherlands in addition to the original project budget.

The Netherlands Delegation agreed to provide the additional funds. Work started on the missiles on 14 October and the task was completed on 21 October. The Contractor's license to export the equipment from Ukraine expired at the end of October, so no time was wasted in demobilizing the operation and returning across the Ukraine border by 25 October.

## 3. COMPLETION OF TASK

The contractor formally handed over the site to the Ministry of Defence in the presence of NAMSA's Representative, Mrs Fisciuc, before leaving. Defence and environmental officials expressed their satisfaction with the work that had been done and with the state of the site. The site was visited by NAMSA in December 2002. All traces of the melanj tank farm had been removed, missiles with decanted and cleaned fuel tanks had been returned to storage and no traces remained of the contractor's operations.

## 4. CONCLUSION

The successful neutralization of the hazards presented by the melanj storage site so close to Chisinau and the prominence given to this by the Moldovan news media enhanced NATO's reputation in Moldova. It also provided a

template for further projects, whether through the PfP Trust Fund or not, to deal with the threat still posed by Melanj storage in many other countries.

The project was completed in 14 months, as planned, and within the budget. A number of lessons were learned that will be of use in the design and execution of future PfP Trust Fund projects.

## **OPPORTUNITIES FOR TECHNOLITHIC TRANSFORMATION OF LIQUID ROCKET FUELS**

Dr. Nariman Javadov

Pilot Industrial Plant of Azerbaijan National Academy of Sciences

Abstract Possibilities for melanj destruction exist within the Republic of Azerbaijan. The Experimental Industrial Plant of the National Academy of Sciences is located within the city of Baku and houses capabilities to process chemicals such as melanj and samine. The EIP contains its own energy source and sewage system and has access to rain lines and other transportation routes. The EIP is already has had success in the petrochemical field developing several plastic and chemical prototypes in its chemical laboratories.

## **1. INTRODUCTION**

We invite you to get know with Experimental Industrial Plant (EIP) of the Institute of Petrochemical Processes, one of the basic enterprises at the National Academy of Science of the Republic of Azerbaijan Center for Joint and Mutually Beneficial Co-Operation.

Experimental Industrial plant of the Institute of Petrochemical Processes of National Academy of Science of Azerbaijan (EIF IPCP NAS of Azerbaijan) is located in the north-east part of Baku City by address : Old Akhmedli, 622 str., House 9 on a land area of about 20,0 hectare.

EIF is the only enterprise dealing with chemical and petrochemical projects in Azerbaijan, and it provides a connecting link between science and production.

The main objectives of EIF are mastering new technologies at practical and experimental industrial standards, recording project indicators of technolithic processes for the future projects. EIF is also involved in building manufacturing and developing preliminary batches of chemical and

petrochemical products of different types, as well as in building and assembling new constructions, their reconstructions, modernization, manufacture of non-standard equipment and other production activities.

## 2. FACILITIES AT THE UNIVERSITY

The following facilities are located on-site at the university:

- 25 experimental and pilot industrial constructions at a total of 3 technolithic workshops
- An experimental industrial and technical workshop employed by the following: field of experimental mechanics, field of power supply and CME, field of transport, and a boiler-house and pump-house
- Plant's laboratory

The experimental mechanic workshop is provided with all necessary metalcutting and mechanical equipment (milling, turning, grinding, polishing), rolls, and hammers.

The plant's laboratory has the capacity to carry out many different analyses by basic types of chemical and petrochemical operations.

There are in-roads to the plant on which are provided an oil cargo pier and capacitance economy (general volume of capacity is 4000m3). Rail branch line can accept 8 tank-wagons at the same time.

## 2.1 Infrastructure of the Facility

The plant is provided with electric power by 2 high-voltage cables (per 10 kilowatt), 3 high-voltage stations and 4 power transformers of general power about 2000 kilowatts.

The plant is permanently provided with drinking and sea waters (section of pump is F 159mm). Besides this there are 2 artesian wells of general production of 5m3/per hour.

Steam supply of plant is provided by boiler-house including 2 Lankashir boilers and 2 boilers E-1/09 working by natural gas. The general production of boilers is 6 t/per hour.

The sewerage system provides for all territories of the plant. All foul waters enter the sewage disposal constructions placed on the exit of plant for mechanical cleaning. After mechanical cleaning, according to the contract with the "Azerneftyag" sewage plant, the foul waters are released to sewage disposal constructions for additional chemical and biological cleaning.

In the technolithic workshops, which have a wide range of available equipment, different operations having to do with chemical and petrochemical fields can be carried out using high pressure and temperature.

## 2.2 Main Achievements of the EIP

The main achievements of EIP in its time of operation have been:

- Development and mastering of progressive system and constructions of reactors with ascending transparent and half-transparent streams
- Labour-rent of process technologies of oligemic divinyl styrene lacquers receiving different marks
- Mastering of process and issuing of preliminary batches of benzonitrile and petroguanamine for production of composite seams, waterproof adhesive, dyes
- Mastering of process of "Super plasticizer NKNS-40-03" developing an effective addition for concrete mixes
- Mastering of process of "Inhibitor of corrosion VFIKS-82 "creating a design for prevention of corrosion and salt deposition on drilling rigs
- Mastering of process of synthetic naphthenic acids , which are used in production of dryers, lacquers, additives to fuels, lacquers
- Additional construction on reception of hydrogen, carbonic acid and nitrogen

## 2.3 Workforce at EIP

Presently employed at the plant are about 120 men, and 40 of them are technical and engineering employees including 10 candidates of technical chemical sciences.

Practically all employees of plant have worked more that 15-20 years and possess of very high knowledge and qualification in their fields.

Starting in the year 2000, EIP is cooperating with the ecological company "Ecoservices" Ltd. During this period, the plant in conjunction with "Ecoservices" has developed effective processes to utilize wastes polluting the environment and at the same time pick out products to be reused. Here are some of them :

• Unique technolithic process of thread locks processing (projectors)

- Technolithic complex on processing of oil and paraffin consisting sludge and also different polymeric waste with receiving of variously oil products (stove fuel, solvent, bituminous composition, cable compound, component for production of grease, clean paraffin and etc.)
- Technolithic process of reconstruction, keeping and utilization of drilling fluid
- Technolothic process (3 stages) of cleaning of reservoir waters and oil consisting sands from heavy metals

This corporation allows for the improvement of the ecological condition of the environment within the Azerbaijan Republic.

## POTENTIAL DANGER OF STORED ROCKET FUEL COMPONENTS AND RATIONAL WAYS OF ELIMINATING THEIR THREAT TO THE POPULATION AND THE ENVIRONMENT

Dr. Fuad Abdullayev

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Abstract The mere presence of melanj and samine in the Republic of Azerbaijan present a danger to the people who work and live near the storage depots. After a preliminary evaluation of the storage depots in October 2003 it was determined that the situation was in need of rapid response. The toxicity of melanj is such that it easily corrodes metals and can begin the harm humans upon coming into contact with mucous membranes. Likewise, samine and isopropyl nitrate pose serious threats to humans as well as the environment.

### 1. BACKGROUND

In military depots in the territory of the Azerbaijan Republic there is a large concentration of the rocket fuel components (RFC) unused since the time of the Soviet Union which, after the lapse of many years of exposure, pose a threat to the environment and population of the neighboring settlements.

For the purpose of estimating the level of danger an operational reconnaissance of RFC storage locations was carried out in October 2003 by the representatives of Azerbaijan National Academy of Sciences jointly with NATO experts (headed by Prof. W.Spyra). As a result of inspection they noted total storage of 1400 tons strong of RFC, the rocket fuel oxidizer mélange, nitric acid AK-20k, AK-27i and AK-27p, as well as 470tons of a rocket fuel TG002, samine and single-component rocket fuel isopropyl nitrate.

The transportation and storage reservoirs used to keep the RFC were noted to be in an extremely threatening state. The degree of decrepitude of the containers makes the whole situation in the regions where the depots are located extraordinary when one takes into account the climatic conditions such as close bedding of subsoil waters and leeward position of the territories. Penetration of RFC into the atmosphere, soil and subsoil waters from depressurized and corroded tanks places guarding personnel and population of nearby settlements under direct threat.

In connection with the statements above, the task of rendering RFC harmless, in the case of the territory of the Azerbaijan Republic and the threat to the people and environment, is of vital importance and calls for a solution in the shortest time.

To carry out a skilled and safe process of rendering RFC harmless inexhaustible knowledge of their properties and shared world experience of their extermination is demanded.

#### 2. MELANJ

The nitric acids RFC stored at the military depots are meant for use as rocket fuel oxidizer. In order to improve the operational properties of the oxidant various additions in mixture with tetraoxide of nitrogen  $(N_2O_4)$  are put into nitric acid.

Proceeding from this, the composition of the stored rocket oxidizer is following:

AK-20k: 80% $N_2O_4$ , 20%  $N_2O_4$ , iodine-containing inhibitor AK-27k: 73% HNO<sub>3</sub>, 27%  $N_2O_4$ , iodine-containing inhibitor AK-27p: 73% HNO<sub>3</sub>, 27%  $N_2O_4$ , fluorine-containing inhibitor

When nitric acid is mixed with water in any ratio, this generates heat to a great extent. Tetra oxide of nitrogen in nitric acid partially dissociates in the formation of nitrogen dioxide ( $NO_2$ ), and this is shown by its brown coloring.

The physical properties of these oxidants are defined by the content of nitrogen oxides and water in them. The principal properties are: coloring from light yellow to brown, density at  $15,6^{\circ}C-1,511-1,575$  g/m<sup>3</sup>, and boiling point of  $66-86^{\circ}C$ .

The mixtures  $HNO_3-N_2O_4-H_2O$  are heavy oxidants, and they interact with an overwhelming majority of fuel substances with inflammation. The nitricbased oxidants are insensitive to stroke and detonation. However, explosiveness is maintained at contact with hydrocarbons as well with spontaneously explosive liquids.

The nitric acid-based oxidizers are highly corrosive substances. They, in practice, interact with all the metals. Some metals interact quite weakly with it, such as aluminum and its alloys, potassium nickel alloyed steels, chrome steels, cast iron and ferrosilicon alloys. As a result of corrosion of storage tank metals and storage equipment being in contact with the oxidant for a long time, the composition of the oxidant changes, it is polluted by the salts, and the storage equipment is destroyed.

The efficient means of cutting the rate of the metal's corrosive dissolution is using corrosion inhibitors, the most effective of which are salts containing iodine or fluorine taken in the amount of 0,4-0,5 %. The military is storing and transporting the nitric acid-based oxidizers in special reservoirs (railway cisterns and tank-lorries and casks) made of aluminum, its alloys or alloyed steel.

The main toxicological dangers of the oxidant to the human body are connected to contact with the skin and mucous membranes, causing severe burns, as well as its penetration into breathing organs, giving rise to inflammatory processes right up to lung edema. The maximum admissible concentration of nitrogen oxides in the air of the working zone is  $5 \text{ mg/m}^3$ . Work with the nitric acid-based oxidizers is carried out in special protective clothing with cowls, gloves, boots and gas-masks. The clothing must be made of acid resisting materials.

In existing experience of annihilation of RFC, particularly, nitric acid-based oxidizers, the process of its catalytic combustion draws one's attention. In this process, oxidation occurs on the surface of the granules of special oxidic catalysts, providing complete conversion of burning materials and preventing formation of nitrogen oxides. Combustion goes on in the air heater type catalytic heat generators, fire places, and catalytic water-heating boilers.

In 2002 the Ukrainian scientific investigations and introduction enterprise Stroom from the city of Vinnitsa carried out a project in Moldova which destroyed 362 t of nitric acid-based oxidizer stored at a distance of 20 km from Kishinev using the process of catalytic combustion.

The enterprise carried-out combustion of melanj within the NATO Partnership for Peace program. With this, \$900 000 US were expended. The process of mélange combustion conformed to the international ecologic legislation and didn't present a danger to the inhabitants of the populated areas, and the indices of atmosphere pollution didn't exceed the admissible standards.

In addition, nitric acid can be destroyed and used in economically profitable projects of utilization with applications in ecologically safe technologies known in common practice.

It is quite obvious that diverse and interesting perspectives are available for the utilization of nitric acid with simultaneous manufacturing of products directed towards agricultural use.

There is already much world experience in producing fertilizers with application of nitric acid. Such fertilizer may be created by processing phosphate rocks to obtaining Nitro-phosphoric fertilizers, and getting Na-K and Ca-saltpeter to obtain granulated ammoniac saltpeter

It is sufficient to note that according to the data of the Ministry of Agriculture of Azerbaijan Republic the annual demand of fertilizers makes up 250 kg/ha.

The Republic arable land being 1,200,000 ha, the annual demand of fertilizers within republic will make up 300 000t.

Proceeding from average expense coefficients (1 t concentrated HNO<sub>3</sub> corresponds to 2,6t of niter) one can obtain 3,500 t of niter from 1,500 t of melanj. When put to utilization in Azerbaijan Republic this will supply  $\sim 10 \%$  of the total need.

In Azerbaijan there is a limitless source of raw limestone and existing wellorganized depots storing the nitric acid rocked fuel oxidizer.

Work carried out in January-December of 1997 under financing by Defense Ministry of the Republic of Belorussia in conformity with the theme within Scientific Research Works (SRW) "Hygenic estimation of soil and plants with use of fertilizers obtained through the utilization of melanj" serves as an illustration of noted considerations on choice of rational economically profitable way of melanj utilization.

Within SRW a study was made of chemical composition, organoleptic properties, biological values and consistency of growth of a 1997 potato

#### Potential Dangers of Stored Rocket Fuels

harvest cultivated by the application of nitric fertilizers obtained by the use of liquid rocket fuel oxidizers like mélange.

According to the Belarussian Scientific-Research Sanitary Hygiene Institute, using nitric fertilizers obtained from mélange has statistically proven to lead to an increase of protein content.

Within this test case, the level of nitrates accumulated in the potato tubers didn't exceed operating regional standards.

In the Republic of Georgia the OSCE has successfully accomplished a project of remaking rocket fuel into agricultural fertilizers. The project was realized by resources from the governments of Germany, Netherlands, Turkey and Great Britain. In addition, Germany sent expert personnel to Georgia. As announced in an OSCE press-release, 400t of the rocket fuel oxidizer mélange, which was deposited on former soviet military base in the western Georgian village of Meria, was remade into fertilizers for agricultural use in the same region.

After finishing the project, Georgian authorities addressed the OSCE with a request to render harmless the other stores of rocket fuel located in the territory of Georgia.

### 3. SAMINE

The rocket fuel TG-02 samine is a mixture of 50 per cent of triethylamine and 50 per cent of xylidine. This fuel is used as a rocket fuel component together with the nitric-acid oxidizer.

Samine is characterized by such physical-chemical properties which provide its safe transportation and storage. It is a transparent liquid from yellow to light brown in color with a boiling point between  $80^{0}$ - $120^{0}$ C.

Samine is included in the range of dangerous and poisonous products. Poisoning by the active fuel may take place by entering an organism through the respiratory ducts and through the skin. As a result of poisoning by samine headaches occur and functions of the central nervous system and eyesight are damaged. Maximum allowed emissions concentrations of samine's components in the air of a working area are (in  $mg/m^3$ ) 3for xylidine , and 10 for triethylamine.

For utter destruction of samine it is possible to incinerate the material using catalytic burning just as with the nitro-acid-based rocket fuel oxidizer described above.

Besides this it is also possible to use it as octane promoting additive to benzene for the increase of octane ratio.

In the USA, England and the USSR during the World War II xylidine was used in the quantity of 2-4 % to benzene as octane enhancer. . Unique characteristics of aromatic amines as additions to benzene include the absence of their reactivity to sulfuric compounds, as well as obviousanti-oxidation properties.

In this respect, it is worth mentioning the Russian elaboration on the usage of nitrogen containing combinations like xylidines instead of ethyl fluid, according to technical conditions number TU 38. 401-58-61-93, with the aim of improving burning stability of benzenes and octane ratio of benzene fractions (an anti-detonation additive). While adding such anti-detonation additives to benzene it is possible to transform benzene AI-80 into AI-92 and AI-92 into AI-95 at a lesser toxicity as compared with TES and manganese additions, and a much better formula of exhaust gas. At present, additives are successfully used at oil-base and oil-processing plants.

## 4. **ISOPROPLY NITRATE**

Isopropyl nitrate, a single-component rocket fuel is a colorless or light yellow transparent fluid with distinctive ethereal smell and is a complicated ether of nitric acid and isopropyl alcohol.

Isopropyl nitrate has the following features: density  $1,02g/sm^3$  at  $20^{\circ}C$  and boiling point of 98-108°C. It dissolves well into organic solvents and less well into water. Isopropyl nitrate is slowly hydrolyzed by alkali solvents and is hydrolyzed more quickly by acidic solvents.

Isopropyl nitrate does not spontaneously ignite at normal conditions, even when put in contact with oxygen, rather it must be ignited from an outside source. It is not sensitive to impact or fraction, doesn't detonate, and burns easily. The flash temperature of isopropyl nitrate is  $12^{\circ}$ C; its vapor with ambient oxygen is exploded in a wide diapason of concentration from 2 to 100% volume.

#### Potential Dangers of Stored Rocket Fuels

Isopropyl nitrate is harmful to the human organism both by breathing the vapor, and upon contact with the skin or the inside of the organism. In mild cases of poisoning the upper respiratory ducts are exasperated, a headache appears, and nausea. In severe cases of poisoning loss of consciousness takes place, which may lead to death. This chemical doesn't cause chemical burning of skin. Maximum admitted concentration of isopropyl nitrate in the air of a working area is  $5 \text{ mg/m}^3$ .

Destruction of isopropyl nitrate can be made by taking into account its easy hydrolyzation by acid solvents.

In addition, it is possible to utilize isopropyl nitrate by using it with the aim of rising the cetane ratio of diesel fuel.

Acquiring the desired cetane number for diesel fuels depends mostly on the selection of crude oil and technology of its refining. However in some cases to improve operating conditions special substances (additives) are added, which improve the cetane number by 16-20 units. Mostly aimed at obtaining diesel fuel fit for winter use, isopropyl nitrate (with an introductory 1.0% by mass cetane number, it increases by 17 units) is in conformity with GOST 305-82.

# TRANSPORTATION OF GENERAL ROCKET FUEL COMPONENTS

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Abstract In order for toxic substances such as rocket fuel components to be safely transported, correct safety measures must be carried out and emergency and first aid equipment must be available. While transporting by a motor column such measures as having empty tanks on hand incase of leakage, an ambulance on hand incase of accidents, and radio contact between all members is mandatory. In addition there must be working place safety measures and fire prevention measures carried out specific to the chemicals melanj, samine, and isopropyl nitrate.

## 1. MODES OF ROCKET FUEL TRANSPORTATION

Transportation of rocket fuel components is carried out by railway, automobile, sea and air transport aimed to keep special rules of transportation and safety engineering. With the purpose of maintaining secrecy and providing security, the rocket fuel components are transported like all types of guarded transport.

While rocket fuel is being transported in containers, the escort is provided (by a consigner) with a hand-operated pump with hoses for oxidant and rocket fuel, with protective clothing, gas-masks, required number of neuralizing agents in suitable containers, a set of tools, a set of gaskets, bolts, nuts, plugs, first-aid kits, means to put out a fire, and an explosion-proof illumination light

Containers and barrels to be filled with rocket fuel components should be filled only to 85% of capacity in summer and 90% of capacity in winter.

Combined transportation of oxidants and rocket fuel by the same means of transport is strongly prohibited, excepting by sea transport means.

By rail, the rocket fuel components are transported in special tankers and in trains in containers and barrels located in truckloads and platform cars, in accordance with the load transportation rules.

AK-class oxidants are transported as a highly dangerous load of "Toxic agents" class in the special tankers, in RA-2 containers and special barrels.

TG-02 rocket fuel is transported as the "Toxic highly inflammable liquids" in the special tankers without lower drainage, in the P-4C steel containers and barrels.

Monopropellant of isopropyl nitrate is transported as a moderately dangerous load of the "Toxic highly inflammable liquids" class in the P-4C steel containers and barrels made of aluminum and steel.

The transported rocket fuel components are to be protected from locomotive, railways carriages and vans loaded with other dangerous cargo. Protection norms and descriptions of load danger (Table 6.1) are mentioned in rail invoice.

## 2. TRASPORTATION OF ROCKET FUEL COMPONENTS BY MOTOR TRANSPORT

The rocket fuel components are transported in special road tankers, motor servicing vehicles, tank trailers as well as in containers and barrels using lorries.

On the left side of the road tanker, motor servicing vehicles with the rocket fuel a red pennant should be attached to be well visible to drivers of oncoming cars.

## 2.1 Restrictions

While the rocket fuel components are being transported it is not permitted:

- To harshly budge, harshly brake and make quick turns
- To exceed admissible speed limits established for these road tankers and motor servicing vehicles
- To reduce distance established between cars and subdivisions
- To be located within the region to be dangerous regarding fire risk
- To produce operations of drainage and filling and eliminate disrepairs while in populated areas

Transportation of General Rocket Fuel Components

- To tow road tankers with rocket fuel for a large distance
- To smoke in cabins and in direct proximity of road tankers, motor servicing vehicles
- To have to sleep or rest in cabins of road tankers or motor servicing vehicles filled with rocket fuel components
- To transport strangers in cabins and backs of cars with rocket fuel

## 2.2 Requirements

Organizing the transportation of rocket fuel by motor transport requires one:

- To organise control of motor transport (MT) columns, these columns' protection, guard and defence
- To provide MT columns with material resources, means of repair and technical maintenance, medical remedies and neutralizing agents

## 2.3 Elements of a Motor Transport Column

The MT columns consist of:

- Road tankers for oxidants;
- Road tankers for rocket fuel;
- Cleansing cars;
- Reserve road tankers;
- Radios;
- Lorries (trailers) to transport rocket fuel in barrels and material resources;
- Road tankers for fuel and lubricants;
- An ambulance.

### 2.3.1 Requirements for Transportation Lorries

Allocated for transportation of rocket fuel components, lorries must fulfill the following requirements.

### 2.3.1.1 While transporting AK-class oxidants

Lorries must be supplied with:

- A hand-operated pump with hoses for each individually proceeding car
- Two such pumps for each column
- Two fire extinguishers for each car

• No less than 200 litres water reserve for each individually proceeding car, no less 2000 litres water reserve for each column

#### 2.3.1.2 While the transporting rocket fuel

Lorries must be supplied with:

- A hand-operated pump with hose for each proceeding car, with two such pumps for each column
- Two fire extinguishers for each car
- 20 litre cans with neutralizing solution for each car
- A box of sand and spade for each car

The first-aid kit should be installed at all cars aimed to transport rocket fuel components.

One or two empty barrels should be loaded on each car when the rocket fuel is transported in barrels. When rocket fuel is transported in tanks, 1-2 cars with empty tanks for oxidants and 1-2 cars with empty tanks for rocket fuel should be included to bring up the rear.

## 3. WORKING SAFETY, TOXICOLOGY AND FIRST AID OF ROCKET FUEL COMPONENTS

## 3.1 Working Area Regulations

AK and TG-02 class oxidants and isopropyl nitrate are strongly toxic agents. The have injurious impact on humans resulting from breathing in vapors, touching the skin and getting into the body. More frequently poisoning takes place as a result of penetration of vapors from rocket fuel components through inhalation.

With the purpose of preventing accidents and preserving health of personnel, all work done with rocket fuel components and special servicing must be conducted in individual protective equipment.

Information of maximum admissible concentrations of oxidants and fuel vapors released into ground water wells is represented in Table 1.

Transportation of General Rocket Fuel Components

Component	Maximum admissible concentration				
	In air of working	In a well with water			
	area,	for sanitary and personal			
	mg/cubic m.	use, mg/l			
AK class oxidants	5,0	10,0 nitrates			
		(of Nitrogen)			
Samine-fuel (TG-					
02):	10,0	2,0			
on triethylamine	3,0	0,5			
on xylidine					
Isopropyl nitrate	5,0	0,5			

Table 1, Maximum admissible concentrations of oxidants and fuel vapors in air and water of	ĉ
wells used for sanitary and personal use	

## 3.2 Toxic Impact of Rocket Fuel Components and First Aid

#### 3.2.1 AK-Class Oxidants

The oxidant vapors may cause poisoning resulted from entering the human organism via respiratory organs and skin.

Reaching the skin and mucous membranes, oxidants may cause different degrees of burns. Damage to the skin is three times as severe with moistened skin in comparison with non-moistened.

Initial signs of high poisoning with oxidants' vapors develop after its impact and are demonstrated in a truckle in nasopharynx, epiphora, cough, feeling of chest constriction, headache, general weakness.

30 minutes-1 hour later initial symptoms will disappear and after the concealed period (period of imaginary well-being) with 3-6 hours or more duration, edema of the lungs may develop, endangering the health of victim. In some cases, initial symptoms of severe poisoning can pass as unnoticed.

After prolonged exposure to oxidants' vapors, the below mentioned symptoms may be observed: parthological changes of mucuous membranes of nose and nasopharynx, damage of nervous system and cardiac-vascular system, changes to the upper respiratory ducts, biochemical changes of blood, reduction of resistance of organism to infections, and more frequent development of chronic diseases of dthe digestive tract.

#### 3.2.2 TG-02 FUEL

This fuel causes poisoning by entering the human organism via respiratory organs, skin and alimentary canal.

Poisoning via respiratory organs can be characterized:

- In mild cases: by headache, chest pain, spittle streaming, nausea, sharp pain in eyesight
- In medium cases: by spittle streaming, sharp pain in eyesight, feeling of suffocation, fits of coughing, pain in chest and stomach area
- In severe cases: by convulsions and toxic edema of the lungs (in addition to other listed signs).

Poisoning through skin and alimentary tract is characterized:

- In mild cases: by a blue colouring of mucous membranes, headache, dizziness, loss of orientation within environment
- In medium cases: by nausea and vomiting (in addition to above listed signs)
- In severe cases: by avomiting, pains in joints and muscles, fits of shivering, partial or full fainting fits, convulsions

The chronic poisoning by the fuel is characterized by headache, dizziness, general weakness, tiredness, disturbance of sleep, memory weakening, irritation, pain in muscles and joints, perspiration, aggravation of eyesight, loss of appetite, diarrhea, pains in a right lower rib, as well as changes in urine chemistry, in functions of liver, and in nervous system.

## 3.3 Isopropyl Nitrate (OT-155)

In mild cases of poisoning, irritation of upper respiratory ducts is developed, as well as headaches and nausea. Reduction of blood pressure joins these symptoms after a more prolonged stay in the proximity of fuel vapors, and eventually anemia is developed..

In severe cases of poisoning, sharp disorders of breathing may be observed, pulse becomes more rapid, skin and mucous membranes get an acute form of blue coloring, the fuel fainting fit comes and can result in death. This fuel does not cause chemical burns.

## 4. THE PRINCIPAL SAFETY MEASURES OF WORKING WITH ROCKET FUEL COMPONENTS

## 4.1 Working Safety

Safety while working with the rocket fuel components can be provided through the application of perfect technical means, individual protective equipment and thoroughly considered precautionary measures. It is easier to prevent accidents resulting from work with rocket fuel than to eliminate its consequences.

While working with rocket fuel components such actions are prohibited:

- The presence of persons not occupied with implementation of mentioned works
- One person to implementing the work alone
- To work without individual protective equipment
- To use the same individual protective equipment in an area where work is being conducted with a different product;
- To continue work in a special dress covered with a chemical agent
- To place samples of rocket fuel components near one's mouth
- While wearing special protective clothing, to visit rooms where the work with rocket fuel components is not conducted
- To use open fire and to smoke on the working place
- To pour off rocket fuel components on the ground, on the floor of working rooms or into household-fecal sewage system
- To conduct work with rocket fuel using non-grounded equipment.

While arranging work with rocket fuel components, possibilities for rapid accident response should be provided such as how to quickly extinguish a fire, to remove and neutralize spilled product and to render first aid for victims.

## 4.2 **On-Site Regulations**

First and foremost, all spilled products are to be immediately neutralized. At spill sites, filling, storage and in pump stations fire extinguishing means must be installed and in working order, in addition to water reserves, neutralizing agents, and first-aid kits.

Working places must be provided with telephone communications, fire alarm systems and systems of point duty.

The inflow-exhaust ventilation with lower and upper drainage - providing multiplicity of air exchange no less than 10-12 volumes per hour - must be installed in closed repositories or other buildings where work with rocket fuel and oxidants is being conducted as well as such ventilation in the pumping stations and laboratory.

Before starting the work, closed repositories - where concentration of toxic vapors and gas could become possible - must be ventilated no less 15 minutes, without fail.

Combined storage and transportation of fuel and oxidants (strengthened hydrogen peroxide, AT, AK classes) in one van (in one car or platform) is not permitted.

An empty reservoir should be left in each storehouse (group of reservoirs) to pour the product into, in a case of leakage. The storehouses, spaces where one works with fuel and oxidants and emergence exists must be maintained free of blockages and in good cleanliness.

## 5. FIRE RISK OF ROCKET FUEL COMPONENTS

AK class oxidants are not burned and blown up. However such oxidants cause spontaneous combustion of a lot of flammable materials (NDMG, TG-02, felt and etc.), and accelerate burning of flammable substances. On prolonged influence the wood vapors of nitric oxides nitratate while harshly increasing inflammable substances.

Rocket fuel NDMG, TG-02, TM 185 and isopropyl nitrate are 1<sup>st</sup> grade highly flammable liquids. Vapors of fuel with air form an explosive mixture. Description of rocket fuel liable to explosion and fire is mentioned in Table 2.

<i>Tuble 2,</i> Description of focket rule hable to explode and me						
Fuel	Flash-	Limits of		Temperature of		
	point	Inflammability		boiling start, (in		
		in the	mixture	degrees Celsius)		
		with air, in				
		volume %				
		Lower	Upper			
Samine (TG-02):	-12	1,5	6,1	86		
Isopropyl nitrate	12	2,0	100,0	93		

Table 2, Description of rocket fuel liable to explode and fire

## CHEMISTRY AND ALTERNATIVE USAGE OF MISSILE PROPELLANTS STORED IN AZERBAIJAN

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Abstract The storage of liquid missile propellants Samine (mixture of xylidine and triethyl amine) and Isonite (isopropyl amine) present a great environmental problem in Azerbaijan. These compounds are no longer in use as propellants. In this paper we will discuss some chemical properties, production and alternative usage of these compounds in industry apart from being propellants and we will give some recommendations for alternative usage with respect to public and environmental safety.

### 1. INTRODUCTION

Propellants are explosive agents which generate large amounts of hot gases by an exothermic reaction without the need of atmospheric oxygen. Propellants are used wherever reproducible, time controlled amounts of working fluid are required to propel rockets and missiles.

The use of propellants started into ancient times for the aim of attacking defense fortifications and ships and also as pyrotechnics for religious purposes. Black powder like compositions were discovered by Chinese alchemist in the eighth century. In the middle of the eleventh century these formulations used as rocket propelled flame throwers. After that nitrocellulose was first synthesized by Schöbein and Böttcher in 1846 and Nobel used nitroglycerine to plasticize nitrocellulose. Prior to the twentieth century the use of rockets propelled by black powder charges was restricted, and the black powder was used just for fireworks and display pyrotechnics. The development of compressed propellant charges containing of smokeless powders began after world War I. Development on propellants was accelerated during the late 1930s and particularly during the war years. The most notable achievements in propulsion of this era were the German liquidpropellant V-2 rocket and the Me-163 rocket-powered airplane. A myriad of solid-propellant technology was also produced. The main advances in

propulsion that were involved in the wartime technology were the development of pumps, injectors, and cooling systems for liquid-propellant engines and high-energy solid propellants that could be formed into large pieces with reliable burning characteristics. From 1945 to 1955 propulsion development was still largely determined by military applications. Liquid-propellant engines were refined for use in supersonic research aircraft, intercontinental ballistic missiles (ICBMs), and high-altitude research rockets. Similarly, developments in solid-propellant motors were in the areas of military tactical rocket applications and high-altitude research. Bombardment rockets, aircraft interceptors, antitank weapons, and air-launched rockets for air and surface targets were among the primary tactical applications.

According to obtained information from Azerbaijani Ministry of Defence, liquid ballistic missile propellants (450 metric tones of Samine -50% triethylamine and %50 xylidine- and 25 metric tones of Izonit-isopropyl nitrate-) that are no longer used by the Azerbaijani forces are stored at two major sites. In this paper we will discuss some chemical properties, production and alternative usage of these compounds in industry apart being propellants and we will give some recommendations for alternative usage with respect to public and environmental safety.

### 2. MAIN COMPONENTS OF SAMINE

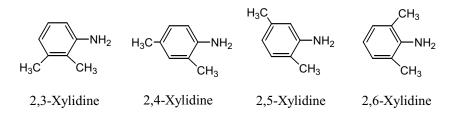
Samine is a mixture of technical isomers of xylidines and technical triethylamine. Samine is used as a fuel component for liquid rocket engines, it is volatile oily liquid with color from yellow to-dark brown and odour is typical of saturated amines. In this chapter we will describe properties, production and usage of Samine's two major components -xylidines and triethylamine.

## 2.1 Xylidines

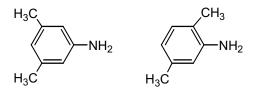
A mixture of xylidine isomers used as a solvent in making lacquers and rubber cement and as an aviation fuel. Xylidines are important precursors for the products, but because of the high carcinogenic nature of some xylidine isomers it becomes very essential and relevant to develop suitable analytical procedures to separate isomers as well as enhance detection at very low concentrations. Micellar electrokinetic chromotography has been standardized at various influencing parameters such as pH, ionic strength and micelle modifiers, and the optimum condition have been ascertained for the best separation and sensitivity of standard mixtures. The applicability of

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procedures in environmental samples is studied. For all xylidines, apart from 3,5-xylidine and, to some extent, 2,6-xylidine, reduction of nitroxylenes is the most important industrial production route. The corresponding nitroxylenes can be obtained by nitration of the pure xylenes. For the reduction of nitro xylidines, processes used in the production of aniline and toluidines can, in principle, be considered.



Xylidines can be used in the dye production. A large number of azo dyes are derived from 2,4- and 2,5- xylidines, whereby the xylidines can function both as diazo and coupling components. Instead of pure 2,4-xylidines, crude xylidines are frequently used to produce red and orange acid dyes. Yellow and orange solvent dyes and some red acid and direct dyes are produced from 2,4-xylidine. An example of an azo dye based on 2,5-xylidine is Solvent Red 26. 3,5-xylidine is curretly almost exclusively used to produce the perylene pigment dye Pigment red 149. Only a few areas of use are known for 2,3-xylidine; e.g., in the form of the amide of 2-hydroxy-3-naphthoic acid, it is a coupling component for azo dyes used in printing inks. The condensation product of bromamine acid with 2,6-xylidine is an intermediate in the production of acidic blue dyes for wool and reactive dyes.



3,5-Xylidine 3,6-Xylidine

2,3-Xylidine is an important raw material of producing Mefenamic Acid which is an anti-inflammatory. It also can be used in the production of dye, pesticide, etc. There is limited evidence on the mutagenicity and genotoxicity of 2,4-Xylidine. The compound is mutagenic in bacteria in the presence of a metabolic activation system. 2,5-Xylidine is an important raw material of dye. It also can be used as an inter-mediate of other chemicals. 2,6-Xylidine is an another important raw material of producing anesthetics. It also can be

used in the production of dye and other chemicals. 3,4- xylidine is a chemical intermediate for synthetic riboflavin. The procedure involves a reductive condensation of 6-nitro-3,4- xylidine with D-Ribose to give the nitro compound, which is catalytically reduced to phenylenediamine. This, when treated with alloxan in acid medium gives riboflavin in 16% yield, based on D-ribose.

Xylidines can be used in the synthesis of polymers. A series of terpolymers were synthesized by oxidative polymerization of aniline, o-toluidine, and 2,3-Xylidine with three monopolymer rations using ammonium persulfate as an oxidant in two acidic media. P-phenylenediamine (PPDA) homopolymer and its copopolymers with 2,3-Xylidine were synthesized by oxidative polymerization using potassium persulfate as an oxidant in HCl medium at room temperature.

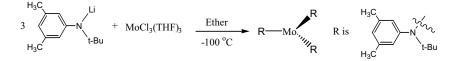
Xylidines can also be used in the plant protection. 2,3-Xylidine is a component of herbicide xylaclor. The insecticide and acricide amitraz is obtained from 2,4-xylidine. 5-Acetamido-2,4-dimethylaniline, which can be obtained by nitration and subsequent catalytic hydrogenation of N-acetyl-2,4-xylidine, is an intermediate in the production of the herbicide and growth regulator methafluridamid, mefluidide. Prowl (Pendimethalin, Penoxalin) is also used as a herbicide and growth regulator. It is obtained from 3,4-xylidine by alkalization and denitrification. 2,6- Xylidine is an interesting precursor for a large number of plant-protection agents. Derivatives of N-choloroacetyl-2,6-xylidine are of interest as herbicides, growth regulators, and fungicides. Commercial products based on 2,6- xylidine are the fungicides metalaxyl and furalaxyl.

The other uses of xylidines are in production of pharmaceutical and pharmaceutical products for veterinary medicine, and vitamins. The antiphlogistic, antirheumatic, and analgesic mefenamic acid is produced from 2,3- xylidines. 2,4- Xylidine is the starting material for the active substance cymiazole, used in veterinary medicine as an ectoparasiticide for combatting ticks. 2,6- Xylidine is a component of a range of similarly structured local anesthetics, such as lidocaine, bupivacaine, mepivacaine, and etidocaine. 2,6-Xylidine is also used in a range of other medicinal products, e.g., the diuretic xipamide, the amidinourea derivative lidamidine hydrochloride, which combats diarrhoea, the arylurea derivative xilobam, which has a tranquilizing effect on the central nervous system, and the coronary vasodilator lidoflazine. The active substance xylazine hydrochloride is also produced from 2,6xylidine, and is used in veterinary medicine as a narcotic and sedative. 3,4-Xylidine is used in the synthesis of riboflavin (vitamin B<sub>2</sub>). It is also precursor in the biosynthesis of vitamin  $B_{12}$ .

The use of xylidines as antiknock agents for gasoline and as antioxidants for lubricating oils and rubber products, has already been mentioned. Xylidines are still added to gasoline as coloring agents, 2,5- xylidine is used as an additive for liguid crystal mixtures. The use of xylidines as corrosion inhibitors in metallic materials has also been described. Xylidines can be used as absorption agents for sulfur dioxide in desulfurizing exhaust gas.

The reaction of formaldehyde with xylidines is analogous to that with aniline, and gives diaminotatramethyldiphenylmethanes and, under hydrogenation conditions, diaminotetramethylmethanes. These products are used as cross-linking agents and hardeners for epoxy reins, or can be further processed to polyurethanes. In 1943 and 1944, xylidines were produced in the United States in large-scale industrial plants.

The  $N_2$  molecule is so unreactive that it is generally considered inert. The usally high stability of nitrogen can be attributed to its large heat of dissociation and the difficulty of oxidizing or reducing nitrogen. Therefore, it is not surprising that in order to produce nitrogen compound it is generally necessary to use energy-rich conditions. Presently, the only commercial process to reduce nitrogen gas to ammonia is the Haber-Bosch Proses. In contrast to the Haber-Bosch Process, the reduction of nitrogen gas by biological systems is conducted in a very economical manner. In nature the enzyme nitrogenase plays a key role in the fixation of nitrogen fixation and photosynthesis are the most important natural processes for food production. Molybdenum xylidene complex can be reduced using tin as a reducing agent.



#### 2.2 Triethylamine

Triethylamine is a member of the alkylamines. This, the most important lower aliphatic alkyl amine in the worldwide market, is a colorless liquid, free of suspended matter and it is miscible with nearly all common organic solvents and with water at temperatures below  $18,7^{\circ}$ C. Triethylamine is a very dangerous fire hazard when exposed to heat, flame, or oxidizers. The vapor form is explosive when exposed to heat or flame. Triethylamine when complexed with nitrogen tetraoxide and undiluted with solvent explodes at temperatures below  $0^{\circ}$ C. This property makes triethylamine the main

component of the rocket fuel (samine). It will cause an exothermic reaction with maleic anhydride at temperatures above  $150^{\circ}$ C. Triethylamine can react with oxidizing materials and, when heated to decomposition, it emits toxic fumes of NO<sub>x</sub>.

Triethylamine has the widest range of uses and is also the most expensive product with respect to the unfavorable distribution of monoethylamine, diethylamine and triethylamine in production. Most of the usage of it are as an organic acceptor in synthesis or as a salt former in precipitation and purification operations. The common uses are; quarternary ammonium compounds for textile auxiliaries, quaternary ammonium salts of dyes, a catalyst and acid neutralizer for condensation reactions, a catalyst for resinbound foundry cores, stabilizer for chlorinated hydrocarbons and vinyl compounds, synthesis of semisynthetic penicillins and cephalosporins and as solubilizers for herbicides in combination with 2,4 dichlorophenoxyacetic acid. In such process triethylamine plays role as a main solvent or intermediate compound.

The largest use of triethylamine (totaling approximately 4000 Mg in 1995) was as a catalyst to cure the resin systems incorporated into sand cores for foundry molds. The cores are produced in what is typically called a cold box or isocure. In this procedure, triethylamine is usually stored in liquid form at room temperature; during its use, it is vaporized into either a stream of air, nitrogen, or carbon dioxide and introduced into the system as a gas. In addition, annually in the U.S., approximately 2,3 Mkg of triethylamine is used as a curing catalyst in phenol-formaldehyde particleboard adhesives; 0,91-1,36Mkg of triethylamine was used for the precipitation and purification of penicillin and cephalosporin antibiotics; and 0,45-0,91 Mkg of triethylamine was used in the interfacial polymerization process for the production of polycarbonate resins. Consumption of triethylamine used as a scavenger of HCl produced during certain reactions, such as during the manufacture of benzyl phthalates from benzyl chloride and monophthalate esters, is limited because triethylamine is recovered and recycled.

Triethylamine is also used as an ingredient in sealing paint (0.5% w/w); in the manufacture of some paper and board adhesives; in reactions, as a stabilizer for the chlorinated solvents perchloroethylene and trichloroethylene, as an anti-livering agent for urea- and melamine-based enamels; in the recovery of gelled paint vehicles; as an accelerator activator for rubber; as a corrosion inhibitor; as a propellant; as a wetting, penetrating, and waterproofing agent of quaternary ammonium compounds; as an emulsifying agent for dyes; for the production of octadecyloxymethyltriethylammonium chloride (textile treatment agent); as an ingredient of photographic development accelerator;

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for drying of printing inks; in carpet cleaners; to solubilize 2,4,5-T in water; in the production of herbicides and pesticides, in the preparation of emulsifiers for pesticides; in nonnutritive sweeteners, ketenes, and salts; and for the desalination of water.

Triethylamine is produced by reacting ammonia with ethanol, N, N-diethylacetamide with lithium aluminum hydride, or ethyl chloride with ammonia under heat and pressure large-scale manufacture of lower aliphatic amines is generally by high-temperature, high-pressure reaction of ammonia and an alcohol over a dehydration catalyst, or over a dehydrogenation catalyst.

 $NH_3 + 3C_2H_5OH \xrightarrow{\text{catalysts}} N(CH_2CH_3)_3$ 

In the first method catalysts include alumina, silica-alumina, silica, titania, tungstic oxides, clays, or metal phosphates. Yields of mixed amines (primary, secondary, and tertiary) from the reaction of ammonia and alcohol in mole ratios of 2:1 to 6:1 are high (" 80% "). The reaction product, comprising water, alcohol, ammonia, and the amines, is treated by continuous extractions and distillations to produce the pure amines. In the second method catalysts include silver, nickel, or copper. By-products include nitriles and amides. Separation of the desired product amines requires extractions and distillations. Less commonly, lower aliphatic amines are produced by treating an aldehyde or ketone with ammonia over a hydrogenation catalyst. Reaction conditions are similar to those second method, but there is a net consumption of hydrogen. Triethylamine is available in bulk quantities from Ashland Chemical Co., Industrial Chemicals & Solvents Division, BASF Corporation, Elf Atochem, North America, and Interchem Corporation. The product is sold by BASF Corporation in tank cars, tank trucks, 55-gal drums, and 5-gal pails.

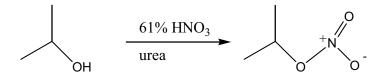
The toxicity of triethylamine in experimentally and occupationally exposed individuals has been evaluated. Severe visual disturbances and changes in electrical activity in the cerebral cortex have been detected in human volunteers exposed to triethylamine by inhalation. Occupationally-exposed workers have reported visual disturbances associated with exposure to triethylamine. Several case reports also indicate that exposure to triethylamine causes ocular and respiratory abnormalities.

### **3.** ISONITE (2-ISOPROPYL NITRATE-IPN)

Isopropyl nitrate is a white liquid with an ether like smell and is known to be a monopropellant of low explosive sensitivity. Isopropyl nitrate also is a volatile liquid with anesthetic properties at lower concentrations as well as causing headaches if inhaled or spilled on the skin.

Isopropyl nitrate can use as the representative nitrate additive ranging from 10, 20, and 50 to 100 mole % in total amount of fuel. Propane and hexane were used as the hydrocarbon fuel in the flame studies and hexane in the ignition delay studies. Shock initiation of detonation and critical diameters were investigated for isopropyl nitrate (IPN). Isopropyl nitrate appears to be ideal for fundamental studies of homogeneous liquid explosives because its long detonation length scale facilitates diagnostics. The initial shock pressure versus the time of detonation and the catch-up time were obtained and the critical shock initiation pressure was determined to be in the range of 7-8.5 GPa at  $0\pm5$  °C.

To prepare Isopropyl nitrate, isopropyl alcohol is nitrated continuosly by adding a mixture of 61% nitric acid with 95% isopropyl alcohol, saturated with urea, into a Florence flask set up for distillation containing boiling 50% nitric acid.



Unlike xylidines and triethylamine, the usage of IPN is not common in industry, as is seen from information give above. IPN can be used as a fuel additive to increase the power of the fuel.

### 5. **RECOMMENDATIONS**

According to obtained information from Azerbaijani Ministry of Defence, there are 450 metric tonnes of the liquid ballistic missile fuel Samine (50% triethylamine and 50% xylidine) and 25 metric tones of Isonite-isopropyl nitrate that are no longer used by the Azerbaijani. Those compounds are a potential risk for human health and the environment. As is seen from information given above especially for xylidines and triethylamine, these compounds are widely used in chemical industry whether as intermediate or

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main compounds (4000 Mg triethylamine usage in 1995). Therefore, a suitable chemical company should be found for these compounds. Unfortunately for Isonite we will suggest to use is as an fuel additive, for oil boiler or diesel engines. These actions must take place in a short time for human and environmental safety.

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## TRANSFORMATION AND COOPERATION: CULTURAL IMPRESSIONS OF AZERBAIJAN

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Abstract After gaining political independence in 1991 Azerbaijan has taken entered into a period of transformation and development. It's people are hopeful for the future and embrace and internationalist approach to their development. The NATO workshop was one such venue for idea-sharing and cooperation in the destruction of military waste leftover from the time of Soviet occupation. This piece shares the author's cultural experience and observations of Baku and of the NATO workshop. The author was able to participate as a researcher funded by the Brandenburg University of Technology in Cottbus and the German Fulbright Commission.

Keywords: Cultural understanding, co-operation, organization, Baku, Azerbaijan, transition, new presidential administration, experiences.

## **1. INTRODUCTION**

My last evening in Azerbaijan, I danced a traditional Azeri dance in a dinnertheatre lounge called *Avilla*. I was joined by colleagues from Germany, Poland and Azerbaijan. Somehow it struck me as a metaphor for post-Cold War Europe. Our group was made up of engineers, scientists, military personnel and a NATO Administrator. Everyone danced together, celebrating a successful week of cooperation and idea-sharing. The Azeris celebrated a positive beginning to their process of demilitarization. I celebrated the joy of having experienced one of the most intriguing weeks of my life.

I took part in the NATO Advanced Research Workshop as an element of my research concerning the environmental and sociological implications of military base conversion and demilitarization. I was funded by the William J. Fulbright Commission in a cooperative agreement between my home government in the United States and my host government in Germany. The

grant supported my time of researching abroad, building cultural bridges and gaining international experience. My year was spent based in Cottbus, Germany, at the Brandenburg University of Technology. My advisor, Prof. Dr.-Ing. Wolfgang Spyra, was a co-organizer of the workshop in Azerbaijan. I was, therefore, not only able to help with organization, but was also a full participant in the workshop myself. Azerbaijan's stores of liquid ballistic missile waste presents a severe hazard, which the workshop aimed to address. A workshop of this type had never been held in Azerbaijan. I was, therefore, present as Azerbaijan made its first steps in the destruction of Cold War era missile waste and began the preliminary stages of demilitarization.

The following article aims to augment these scientific proceedings with an experiential cultural analysis of my time in Azerbaijan. In no way do I consider myself an expert on Azerbaijan or its people, rather I wish to provide information about the workshop from a different vantage point and to introduce the country of Azerbaijan as I experienced it.

### 2. AZERBAIJAN

Baku was a timely setting for the workshop, considering the stage of transformation Azerbaijan faced at the end of 2003. In October of 2003, Ilham Aliyev, the son of the former president Heydar Aliyev was elected president. It was the first time in a former Soviet Republic that the office was passed from father to son. The Organization for Security and Cooperation in Europe criticized the validity of the election. Nevertheless, Ilham Aliyev took office and committed to help continue the process of development in Azerbaijan. One part of this development is the construction of the Baku-Tbilisi-Ceyhan oil pipeline. The massive oil channel originates off-shore of Baku in the Caspian Sea, and is projected to be finished in 2004. With its completion, Azerbaijan can expect its oil revenues to increase considerably. This sets an optimistic forecast for economic development in the country.

While taking a walk through the city, the dynamism of Baku and diverse cultural history was palpable. The Absheron Peninsula, on which Baku is situated, was first settled in 8000 B.C.E. by hunter gatherers from the Caucasus Mountains. The oldest parts of Baku City are situated not far from the shores of the Caspian Sea, including the *Giz Galazi*, the Maiden Tower, which was constructed in the sixth century B.C.E.. According to legend, a betrothed maiden was locked in this tower to be kept from suitors before her marriage. In the old town of Baku, one sees evidence of the ancient Persian culture in the "antique" tea urns and oil lamps sold in street markets. Carpet

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dealers beckon passers-by into dimly-lit rooms filled with colourful Azerimade tapestries and fine carpets. Dealers explain the regional patterns and colours used, and boast of the quality and superiority of the Azeri-products. Inside the ancient city walls one can dine in a restaurant, the *Karavansary*, built as lodging quarters for travellers on the Silk Road. I myself travelled three times to the *Karavansary* for dinner, and enjoyed lamb kebap, nut kebap, sturgeon, and other traditional Azeri foods. Strains from an Azeri folk music trio drifted through the courtyard of the restaurant and on one occasion, a belly dance appeared for a guest performance.

Outside the sheltered walls of Old Town Baku scores of Russian Ladas and Volgas whiz by at breakneck speed, navigating their way through Soviet-era prefabricated-slab apartment buildings. The modern city centre boasts, among other shops and restaurants, a Holiday Inn, several Internet cafés and the omnipresent sign of capitalism: McDonalds. The contrast of old and new, east and west, and communist and capitalism prove that this city is well acquainted with change. Traces of past regimes and cultural influences are visible not only in the architecture of the city, but also in the lifestyles of the citizens.

Above all others, the Russian influence is still the foreign influence felt most strongly in Baku. Products from Moscow are imported and most citizens are fluent in the Russian language. Nevertheless, merely 13 years after Azerbaijan achieved its independence. Western influences have found a firm place here, spurred-on by foreign interests in natural resources. Shell and BP both have posts in Baku and Lufthansa and British Airways both fly directly to Baku multiple times weekly.

Azerbaijan is a bountiful and fertile land. Natural resources seem to be spilling out of every region of the country. It is clear that Azeris have abundant oil supplies. This becomes evident simply by driving through the outskirts of the city, where oil wells spring up out of gardens and the smell of crude oil hangs thick in the air. Less apparent, however, is that Azerbaijan could largely be self-efficient in agriculture, provided the proper infrastructure is in place. Because of its geographical location, Azeri farmers enjoy two growing seasons. Citrus fruits, vegetables, tea and countless other produce items are grown and sold within the country. I was told by one Azeri woman that there are over 20 different types of olives that grow in Azerbaijan. The land is so suited for olives that vines grow out of the cracks in the sidewalks!

Managing these natural resources will be the challenge of the new presidential administration inaugurated with Ilham Aliyev. In Soviet times, when Azerbaijan was seen as a vacation destination and bread basket for Russia, the

country's natural resource revenue disappeared into corrupt dealings and money laundering. With this new democratic government, and a state-run oil company, the required apparatus is in place to properly manage the country's revenue. The challenge for the new president, who happens to be the former vice-president of the State Oil Company, will be to fight corruption and deliver the benefits of Azerbaijan's natural resources back to its people.

## 3. UNDERSTANDING PEOPLE

The Azeri people anticipate future progress and are hopeful that under new governance the oil revenue will serve to help their country's development. It is the people's responsibility, I was told by one Azeri major, to take care of their country, to nourish it and make it thrive. I found the Azeri people to be very proud of their country in a way that I imagine the early American settlers were proud of their new land. Unlike the early American settlers, though, who set off to be independent in their new domain, the Azeri people embrace international relationships and co-operation. The growing quantity and popularity of the Internet in Azerbaijan is a tell-tale sign that the next generation will grow-up computer literate and able to contribute to the global technological scene.

The NATO workshop offered another way for the Azeri people to connect with global information resources. This gathering of scientists, military personnel and government administrators was not only an opportunity to share ideas and experience, it was also an opportunity to share cultural practices, tell stories and learn from one another's world views.

As a young American who grew-up with films portraying the ever-suspicious Soviet adversary, I was happy to have all stereotypes disproved at the NATO Workshop. It was a first time experience for me to work along-side workshop participants from Azerbaijan, Estonia, Kazakhstan, Uzbekistan, Tajikistan and Georgia. Here I found myself shaking hands with scientists from around the world whose work I had encountered in my research. The week began with an opening ceremony where participants gathered for the first time to share a meal. I knew after the group's first gathering that the week was going to be enlightening on several different levels.

#### 4. WORKSHOP EXPERIENCES

On the night of the opening ceremony, we gathered at a large table loaded with plates of flat bread, green herbs, tomatoes and goat cheese. Bottles of water, juice, wine and vodka were present in abundance. The guests exhibited varying degrees of lack of sleep and lack of interest. I sat there, first not knowing the identities of the strangers seated around me and second not knowing in which language I should try to converse with them. Although I had helped with the organization of the workshop, writing emails and faxes to the various participants, I had never had the chance to connect faces with the names. Feelings of uncertainty dissolved, however, when our two coorganizers stood-up at the front of the table and called the group to attention. The first order of business was to fill the glasses with vodka and make a toast. Thereafter, a toast was made every five minutes and food seemed to arrive at the table in an unending stream. Of course we were expected to raise our vodka glass and drink with every toast. Empty vodka glasses were quickly refilled. Being unaware of how many toasts were yet to come, and wishing to stay coherent for the duration of the evening, I learned to carefully ration the amount of vodka I kept in my glass.

Giving toasts in Azerbaijan is an art with intention, as it provides a means to recognize all the guests sitting at the table. We toasted those from the Central Asian Republics, those from Germany, from Azerbaijan, from Poland, from Estonia and so on, until every person sitting at the table had been recognized and introduced. As dictated by Azeri custom (which was adopted from the Russian custom), the third toast of every meal is made to women both present and non-present. When there are women present at the meal, the men must stand during the toast as a sign of respect and appreciation. Being the only woman at the table that evening, I remained seated and absorbed the full intensity of twenty-some men raising their glasses to the women in their lives and to me, who could only sit and watch.

I found it a bit flattering, a bit embarrassing and quite amusing to be saluted in such a way. I imagined how some American or European women would feel uncomfortable being singled out as women, being saluted, but being expected to sit while the men stood. It was clear that the position of women in Azerbaijan was different than that in Europe or the United States. Although Azerbaijan is 97% Muslim, the country approaches religion very liberally, which is evident in their enthusiastic consumption of alcohol. I was in Baku for the final day of Ramadan. It was a national holiday and the children had the day off from school, but other than a recording of a morning prayer

broadcasted over the city from the minaret of the mosque, life in the city continued as normal.

Out of nearly thirty participants at the NATO workshop, there were two women: myself and Wendy Carrick from the United Kingdom. As one of the only women, I was given a larger room to sleep in, and it was expected that my suitcase would be carried for me to and from the car. Trying to refuse these services was seen as rude. I noticed a degree of discomfort when I extended my hand to shake hands with an Azeri man. At first it didn't occur to me that they were resistant to shake my hand. Gradually I noticed, however, that if I were standing in a group, approaching newcomers would offer their hand to every man in the group, but not to me. I asked Ahmet Gizir, a participant from Turkey, why this was and I learned that the practice of not shaking a woman's hand goes has its roots Islamic teachings, and has remained practice as a cultural habit. For me to offer my hand in greeting would usually be accepted, though seen as a bit strange or uncomfortable. I tried to co-operate with the cultural practices in Azerbaijan as best I could. I adjusted to the flow of the day, remembered not to force anyone to shake my hand and was careful each evening with my bottomless glass of vodka. On the night of the closing ceremony, however, Ms. Carrick and I could not resist the temptation. We stood-up, held our glasses high and as the rest of the table sat and watched, we proposed a toast to the men in our lives.

The workshop itself was a product of cultural cooperation. Organization had been a joint effort by the Prof. Dr.-Ing. Spyra and the Azeri chemist and professor Ayaz Efendiyev. Each man approached the organizational tasks in a different way. While one co-organizer preferred details to be set and determined ahead of time, another tended to remain flexible and make adjustments to the plan as the situation dictated. Although this sometimes led to conflict, the overall result was a well put-together workshop which was beneficial to the participants.

Cultural miscommunications did arise, however, and these often served as comic relief for the participants of the workshop. One such case occurred when the group made a visit to the depot where the chemicals melanj and samine were stored in Alyat. As understood by co-organizer Spyra, the participants would be riding in a large Mercedes bus, which would accommodate comfortably the group of 27 and deliver us to our destination with ease. The vehicle which actually arrived, however, was a Mazda minibus. This minibus had the amazing ability to produce seats out of every ledge and corner of its interior. As our group loaded into the bus, seats continued to appear until everyone had found a place, albeit a snug one (see Photo 1). We

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arrived safely to our destination, conducted our visit and still had time to share tea, cookies and conversation with the Alyat officers.



Photo 1, NATO Participants on the way to the Alyat depot. Photo from Wendy Carrick.

Under NATO regulations, all meetings and proceedings must be conducted in the English language. This is a practical way of eliminating language barriers among people from several different countries. The problem at our workshop was, however, that the majority of the participants had been educated in the former Soviet Republics where Russian, rather that English was the preferred language. Nevertheless, according to regulations, our workshop was conducted in English. This may not have been the most productive means, however, because it effectively excluded a section of the group from active participation. Although there were translators available to translate English into Russian or vice versa, these interpretations were only occasional and never absolutely complete. Proof of this was the tired expressions on many participants' faces after a long day of discerning meanings out of partially understood sentences.

Fortunately, participants conducted additional discussions on the topic disposing of the chemicals melanj and samine outside the conference room setting. Many lively discussions were held during tea breaks and meal times.

The forum of discussion outside of the formal meetings ensured that all participants were able to express their views, add their knowledge, and make known their preferential disposal option for the liquid ballistic missile wastes.

## 5. CONCLUSION

This experience in Azerbaijan was a lesson in flexibility and trans-cultural understanding. It was also a rare opportunity to be involved in Azerbaijan's preliminary stages of demilitarization. Azerbaijan will encounter growing pains and challenges in its emersion as an independent nation. Nevertheless, the people are hopeful for the future and are open to international cooperation. As a student of ecology I have learned look at situations as systems of relationships with nourishment and energy flowing throughout. Applying this concept to the NATO workshop, I clearly see how scientific knowledge can flow from one country to the next and how this knowledge and shared experience can serve as nourishment for the growth of constructive undertakings. The experience I gained participating in the workshop, as well as those gained drinking tea at cafés along side the Caspian Sea are also nourishment for my own future in cultural understanding and academic networking. I look forward to following Azerbaijan's process of emergence and value the lessons I gained participating in this phase of its history.

In closing, I would like to share a word of thanks to those who helped make this experience possible and especially those at the Brandenburg University of Technology in Cottbus and the Fulbright Commission for supporting my studies this year.

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**NATO Advanced Research Workshop** *November 25-29, 2003: Baku, Azerbaijan* 

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