MONTREAL PROTOCOL
ON SUBSTANCES THAT DEPLETE
THE OZONE LAYER

UNEP

REPORT OF THE
HALONS TECHNICAL OPTIONS COMMITTEE

DECEMBER 2014

TECHNICAL NOTE #4

RECOMMENDED PRACTICES FOR RECYCLING
HALON AND HALOCARBON AGENT ALTERNATIVES

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The text of this report is composed in Times New Roman

Co-ordination:	**Halons Technical Options Committee**
Composition of the report:	**Halons Technical Options Committee**
Reproduction:	**UNEP Ozone Secretariat**
Date:	**December 2014**

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UNITED NATIONS ENVIRONMENT PROGRAMME

Ozone Secretariat, P.O. Box 30552, Nairobi, Kenya

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ISBN:

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Acknowledgements

The UNEP Halons Technical Options Committee (HTOC) acknowledges with thanks the outstanding contributions from all individuals and organisations that provided technical support to Committee members.

The opinions expressed are those of the Committee and do not necessarily reflect the views of any sponsoring or supporting organisations.

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Table of Contents

Preface

Technical Note #4, *Recommended Practices for Recycling Halon and Halocarbon Agent Alternatives*, replaces the chapters on this subject that have been part of previous Assessment Reports of the UNEP Halon Technical Options Committee (HTOC). Future reports, including the 2014 Assessment Report, will contain an abbreviated chapter that briefly introduces the subject of *Recycling Halon and Halocarbon Agent Alternatives* and refers the interested reader to this document. The HTOC elected to take this approach as much of the information that, while important to understand when developing strategies for recycling halons and alternatives, has been largely reported in prior editions of the Assessment Reports, which contained few changes or updates. As such, it was deemed by the HTOC to make the *Recycling* subject a stand-alone document that is referenced by future Assessment Reports. By this approach those having particular interest in the technical aspects of the *Recycling* subject can access a self-contained document.

1.0 Introduction

Prior to the halt in production of halons, replenishment agent to recharge extinguishers and extinguishing systems had a fairly simple supply chain from manufacturer to servicing company to the end user. With such a short supply chain the quality assurance needs of all parties were readily achieved; or, in the rare case of out of specification agent, problems were easily traced back to the source and corrective action taken.

Today we no longer have newly manufactured halons and the fire protection industry must rely on "used" halons for the recharge of extinguishers and extinguishing systems. In the case of halocarbon[1] clean agents, while they are still being manufactured, the bulk of replenishment agent used for the recharge of extinguishers and extinguishing systems is from systems or extinguishers removed from service. That being the case, the industry faces the same challenges in ensuring the quality, especially purity, for both halons and halocarbon clean agents used for replenishment. The source of replenishment agent has thus shifted from a handful of agent manufacturers around the world to literally millions of end users who own extinguishers or extinguishing systems who may at some point offer the agent up for recycling. Furthermore, the condition of the agent at its entry (or re-entry) point into the market has shifted from newly manufactured agents with an extremely high level of purity to "used" agent that can have any of several types of impurities.

2.0 Standard Methods of Halon Treatment

In the fire protection industry there are several terms used to describe the treatments of halons and halocarbon clean agents to prepare them for possible redeployment:

[1] Halocarbon agents are halogenated hydrocarbon chemicals, including hydrochlorofluorocarbons (HCFCs), hydrofluorcarbons (HFCs), perfluorocarbons (PFCs), a fluoroketone (FK), and a fluoroiodocarbon (FIC), that are used for fire-fighting applications.

- **Reuse**: To remove agent cylinder or extinguisher from one application and re-install in another application.
- **Recover**: To remove agent in any condition from an extinguisher or extinguishing system cylinder and store it in an external container without necessarily testing or processing it in any way.
- **Recycle**: To clean recovered agent for reuse without meeting all of the requirements for reclamation. In general, recycled agent has its super-pressurising nitrogen removed in addition to being processed to only reduce moisture and particulate matter.
- **Reclaim**: To reprocess agent to a purity specified in applicable standards and to use a certified laboratory to verify this purity using the analytical methodology as prescribed in those standards. Reclamation is the preferred method to achieve the highest level of purity. Reclamation requires specialised machinery usually not available at a servicing company.

For the purposes of this chapter, the expression “recycle” is intended to include both the “reclaim” and “recycle” treatments described above.

In order to have a credible agent resupply industry, the “used” agents must be properly processed in order to remove impurities and return the agent to a purity level consistent with newly manufactured agent. Furthermore, the participants in the agent resupply industry must have the technical ability to test and certify that the agents being offered for replenishment are indeed free of impurities. Without that ability rigorously applied, there can be no credible halon or halocarbon clean agent resupply industry.

3.0 Specifications for Agent Treatment, Testing and Certification

The most common halocarbon clean agents in use today are:

- HFC-23 (trifluoromethane)
- HFC-125 (pentafluoroethane)
- HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane
- HFC-236fa (1,1,1,3,3,3-hexafluoropropane)
- FK-5-1-12 (dodecafluoro-2-methylpentan-3-one)

The requirements for these halocarbon agents are contained in NFPA 2001 [see reference 1] and the ISO 14520 series of standards [see reference 4]. The requirements for halons 1211 and 1301 are contained in ISO 7201-1, [see reference 2], and for halon 2402 are contained in GOST 15899-93, [see reference 3]. The requirements are summarised in Table 1.

Table 1: Requirements

Property	Requirements			
	Halocarbons (1)	**Halon 1211 (2)**	**Halon 1301 (2)**	**Halon 2402 (3)**
Purity, % (mol/mol)	99.0 min	99.0 min	99.6 min	99.5 min
Acidity, ppm by mass	3.0 max	3.0 max	3.0 max	
Water content, ppm by mass	10 max	20 max	10 max	30 max
Non-volatile residue, % (mol/mol)	0.05	0.01	0.01	
Halogen Ion		Passes test	Passes test	
Suspended matter or sediment	None visible	None visible	None visible	

Note 1: According to NFPA 2001
Note 2: According to ISO 7201-1
Note 3: According to GOST 15899-9

The following are some suggested procedures for testing for the requirements in Table 1:

- **Purity:** Determine the purity by gas-liquid chromatography (GC), using generally accepted laboratory techniques. If this test indicates the presence of unidentified impurities, then determination by gas-liquid chromatography/mass spectrometry (GC/MS) is recommended.
- **Acidity:** Determine the acidity by the appropriate method specified in ISO 3363. [see reference 5].
- **Water content:** Determine the water content by the orthodox Karl Fischer method [see reference 6] or by any other method giving equivalent results.
- **Non-volatile residue:** Determine the non-volatile residue by the method specified in ISO 5789, [see reference 7].
- **Halogen ions:** Mix 5 g of the sample with 5 ml of absolute methanol containing several drops of a saturated methanolic silver nitrate ($AgNO_3$) solution. The resulting solution shall exhibit no turbidity or precipitation of silver halide.
- **Suspended matter or sediment:** Examine the liquid phase of the sample visually.

4.0 Agent Contamination

The presence of agents of questionable purity is an insidious problem that does not become apparent until an end user discharges an extinguisher or extinguishing system, often in a serious life safety or potential property loss setting. With an impure agent the performance can range from poor or no fire extinguishing effectiveness to one where the impure agent may actually intensify the fire in the case where the impurity is a flammable material.

Generally speaking, end users do not have the means to confirm the purity of replenishment agents they have employed in fire extinguishers or in extinguishing systems. Instead they have had to rely on the aftermarket supply chain to collect, process, test and certify that the agent is of acceptable purity. From the end user's perspective, it is that last step – the certification – that has been the ultimate basis for acceptance of the agent. Given that there has been at least one

instance where a certification was allegedly falsified by the agent supplier, it would seem that relying on a supplier's certification alone can introduce risk with respect to agent purity.

To understand how and/or why agents with impurities can be supplied to end users, one has to look at the circumstances under which the impurities can be introduced. For all practical purposes the impurities are usually introduced into the agent in four different manners. First, the impurities could already be present in the agent when the recycler or servicing company received the agent or the extinguisher containing the agent from an end user or intermediary. Second, the agent could become contaminated during processing by the recycler or servicing company when "good agent" is accidentally batched together with contaminated agent, thus causing the entire batch to become contaminated. This is referred to as 'cross contamination with other halocarbons.' Third, the failure to adequately deep vacuum the equipment when changing from processing a different agent or refrigerant will cause the introduction of impurities by cross contamination with other halocarbons or the introduction of other contaminants including oil, moisture, particulates or acids. Finally, agent that has been reclaimed to a standard can still be contaminated if it is put into cylinders or long term storage tanks that have not been properly cleaned, and which contain contaminants such as water, oil and particulates.

5.0 The Agent Supply Chain

Figure 1 illustrates the parties involved in the supply chain for recycled halons and halocarbon agents.

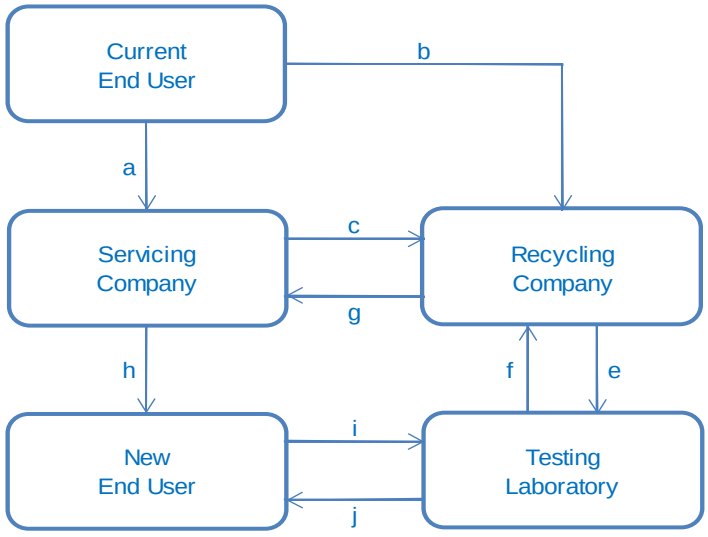

Figure 1: Supply Chain for Halon and Halocarbon Agent Recycling

In the trading of recycled halons and halocarbon agents, there are usually five parties involved in commercial transactions:

- The current end user of the agent or extinguisher sells the contents of its extinguishers or extinguishing systems. This sale is usually to either a servicing company (a) or to a recycling company (b).
- The recycling company buys the agent or extinguisher for processing the agent and returning it to the required purity level and other testing requirements. The recycling

company could buy the agent from the current end user (b) or from a servicing company (c).

- After processing the agent the recycling company has the agent purity confirmed by a testing laboratory (e to f). This laboratory is often a third party organisation and in other cases it is part of the recycling company.
- In most cases the recycling company sells the recycled agent to a servicing company (g) for use in recharging the extinguishers of a new end user (h). In some cases the current end user and the new end user could be the same with the agent being processed and then banked for the end user. The banking service is sometimes provided by the recycling company and in other cases by the servicing company or by the new end user itself.
- Although the recycling company should provide complete certified test reports with each tank or batch of agent sold, from time to time the new end user may deal with the testing laboratory directly to have a sampling of its extinguishers contents tested to confirm that the agent therein is up to specification (i to j). In some cases the new end user employs the servicing company as an intermediary with the testing laboratory.

There are instances where the services of a recycling company and a testing laboratory are not part of the process. That is when the servicing company merely recovers agent from the extinguishers or extinguishing systems of a current end user and then reuses that agent to recharge the extinguishers of a new end user (a to h) with little or no purification efforts and no testing. This is considered poor practice because one is never certain about either the contents or the purity level in the current owner's extinguisher and there is no provision to identify any contamination introduced in the transfer process. Thus, extinguishers and extinguishing systems recharged with agent by this simple method have no credibility with regard to meeting purity or testing standards and thus performance effectiveness may be compromised. In many nations, this practice is prohibited by law or regulation.

In the case of halon 1301, recycling companies often use a 'halon identifier' instrument; see reference [8], to determine the percentage purity of newly received halon in order to prevent contamination of other halon when combined in a batch.

Depending on the purity of the agent when received for recycling, reclamation efforts by the recycling company may be as simple as nitrogen separation and filtration. If, however, cross contamination with other halocarbons or volatile residues is found, then the agent mixture must be submitted to a distillation process to return the agent to a condition meeting the requirements of the appropriate standard. In some cases it may not be economically feasible to "clean" the agent depending on the type and degree of cross contamination.

6.0 Agent Contamination Mitigation Strategies

In reviewing the supply chain for recycled halon and halocarbon agents, it is clear that the minimum mitigation strategies that can be employed to ensure that the agent meets an industry accepted quality standard are:

- **By the Recycler**: Employing robust quality assurance procedures that provide for (1) testing incoming agent to ensure that it is not contaminated before it is combined with other batched agents during the recycling process; (2) processing the batched agent in a

manner to remove all contaminates to the specified levels, ensuring that no new contaminants can be introduced into the processed agent up through and including its final storage condition (cylinders, long-term storage tanks, drums, etc.)

- **By the Testing Laboratory**: In accordance with good laboratory practice, perform an analysis on samples of the recycled agent for each individual storage container (cylinder, drum, etc.) and provide written certification that the agent meets the required specifications. See Table 2 for a list of laboratories that may be considered for performing testing and certification.
- **By the Servicing Company**: Preparing and following established, good practices when recharging extinguishers and extinguishing systems to ensure no contaminants are introduced at this stage either by the agent transfer equipment or by improper cleaning and drying of the extinguisher cylinder.
- **By the New End User**: Periodically removing extinguishers from service and having the contents analysed by a testing laboratory to check for contaminants in the contents. This can be done in a cost effective manner by applying standard statistical sampling methods.

Table 2: Testing and Certification Laboratories

NIPPON EKITAN Corporation Kanto Gas Center Kiyoku-cho 1-2, Kuki, 346-0035 Saitama Japan Phone: +81 480 23 1313 Fax: +81 480 23 1329
Kansai Gas Center Murotani 2-1-3, Nishi-ku, Kobe, 651-2241 Hyogo Japan Phone: +81 78 991 7839 Fax: +81 78 991 7840 Website: http://www.n-eco.co.jp
Meridian Technical Services Ltd 14 Hailey Road, Erith Kent DA18 4AP United Kingdom Phone: +44 0208 310 3911 Fax: +44 0208 310 5687 Website: http://www.meridiantechnicalservices.com
Hudson Technologies (Headquarters) (1) PO Box 1541 One Blue Hill Plaza Pearl River New York, NY 10965 USA Phone: +1 845 735 6000 Website: http://www.hudsontech.com

Table 2: Testing and Certification Laboratories

Hudson Technologies (Headquarters) (1) 3402 North Mattis Avenue Champaign, Illinois 61821 USA Phone: +1 217 373 1414 Website: http://www.hudsontech.com
National Refrigerants Laboratory (1) Inc. 661 Kenyon Avenue Bridgeton, NJ 08302 USA Phone: +1 800 262 0012 Phone: +1 856 455 2776 Website: http://www.refrigerants.com
A-Gas RemTec (1) 1100 Haskins Road Bowling Green, OH 43402 USA Phone: +1 419 867 8990 Fax: +1 419 867 3279 Website: http://remtec.net
Intertek ETL Semko (2) 1717 Arlingate Lane Columbus, Ohio 43228 USA Phone: +1 614 279 8090 Website: http://www.intertek.com/hvac/refrigerants/halon-analysis

Note 1: These laboratories are AHRI (Air-Conditioning, Heating and Refrigeration Institute) certified to analyze refrigerant products, and because of product similarity, are also acceptable to the U.S. Department of Defense (DOD) for halon analysis.

Note 2: Although not identified as a certified laboratory, the U.S. DOD has utilized and accepted analyses provided by this laboratory.

7.0 References

1. "NFPA 2001 – Standard on Clean Agent Fire Extinguishing Systems – 2012 Edition," National Fire Protection Association, Quincy, MA.
2. "Fire Protection – Fire Extinguishing Media – Halogenated Hydrocarbons – Part 1: Specifications for Halon 1211 and Halon 1301", ISO 7201-1; Second Edition: 1989.
3. GOST 15899-93, Specification for 1,1,2,2-tetrafluorodibromethane (R-114B2).
4. "Gaseous Fire Extinguishing Systems – Physical Properties and System Design – Part 1: General Requirements, ISO 14520-1:2006(E)."
5. "Fluorochlorinated Hydrocarbons for Industrial Use – Determination of Acidity – Titrimetric Method, ISO 3363:1976."
6. "Determination of Water – Karl Fischer Method (General method) – ISO 760:1978."
7. "Fluorinated Hydrocarbons for Industrial Use – Determination of Non-Volatile Residue, ISO 5789:1979."
8. One such instrument is shown at http://www.refrigerantid.com/halon/identifier.html.