

Ozone Depleting Solvents Phase-out in Small Size Enterprises in Romania



For additional information and ordering of brochures:

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Montreal Protocol

Montreal Protocol on Substances that Deplete the Ozone Layer, adopted in 1987, establishes specific limits on production and consumption levels and deadlines for total elimination of ozone depleting substances listed in this one annexes. The Protocol was amended in London in 1990, in Copenhagen in 1992, in Montreal 1997 and in Beijing in 1999.

The solvents controlled by the Montreal Protocol are: chlorofluorocarbons (i.e. CFC-113, trichlorofluoroethan), carbon tetrachloride (CTC), methyl chloroform (MCF - only 1,1,1-trichloroethane) and hydrochlorofluorocarbons (i.e. HCFC-225, HCFC-123, HCFC-141b).

In Romania, the solvents were used for: *metal degreasing* (bearings, metallic surfaces cleaning and cleaning of production and transport oxygen equipments), *textiles dry cleaning*, *cleaning / degreasing of electronic components*. Laboratory applications, considered as essential uses and use as process agent (for some technological processes) are still permitted by Montreal Protocol.

The implementation of Montreal Protocol provisions in Romania lead to: CFC-113 used in electronics was replaced by alcohol based solvents or by perchloroethylene; MCF has not been produced since 1997 and has not been used since 2002; the consumption of CTC has drastically decreased, and HCFCs use is forbidden.

Carbon Tetrachloride (CTC)

Carbon Tetrachloride is the only solvent regulated by the Montreal Protocol which is still used in Romania, being regulated by Law no.159/2000.

Discovered in 1839 CTC is a very effective chlorinated solvent that became popular for metal degreasing from the late 1890s and as a dry cleaning solvent (to replace flammable solvents) in the 1930's.

CTC is a heavy, colorless liquid at normal temperature and pressure and has a distinctive odour. Its boiling point is 76.5°C and it is non-flammable. It is a powerful solvent and it mixes with most organic liquids including ether, chloroform, benzene a/o. It does not mix with water. It is the cheapest of all chlorocarbon solvents. CTC classification as very toxic and probably carcinogenic chemical, determined its replacement in the late 1950's.

In the stratosphere, CTC molecules break down under solar UV radiation and release their constituent chlorine atoms. Because of ozone high reactivity and of cascade reactions, one chlorine atom can destroy nearly 100 000 ozone molecules, on average.

Stratosphere Ozone layer depletion allows harmful UV-B radiation to strike Earth. Excessive UV-B radiation leads to: more skin cancers and eye cataracts, less productivity of plants, loss of immunity to diseases and adverse effects on plastics. CTC was included as a controlled substance under the Montreal Protocol through London Amendment in 1990.

Cleaning Alternatives

Ozone depleting solvents are bulk chemicals, in their transport containers, or mixtures containing more than 1% of this kind of solvents. In accordance with the Vienna Convention for the Protection of the Ozone Layer definitions, alternative substances means substances which reduce, eliminate or avoid adverse effects on the ozone layer.

Traditional cleaning agents include: hydroflouorocarbons, hydrochlorofluorocarbons, perfluorocarbons, chlorocarbons, oxygenated solvents, and hydrocarbons.

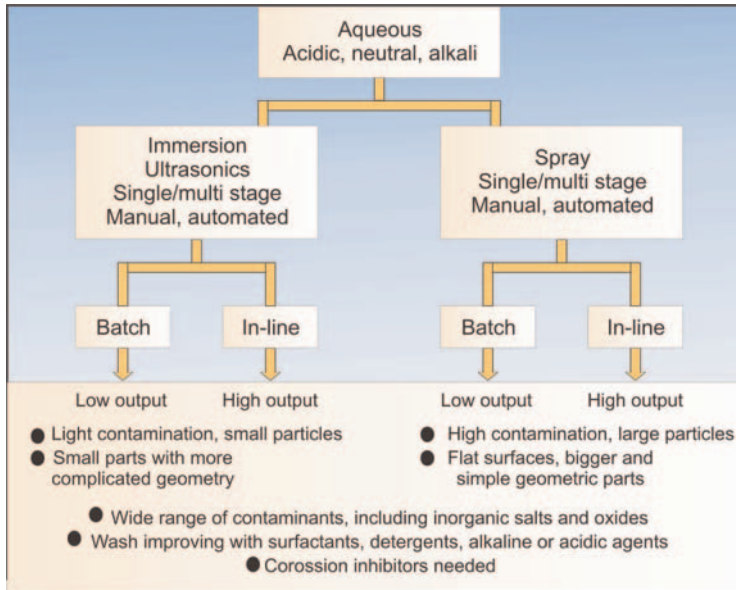
The "ideal" cleaning agent should have the following characteristics: non-flammable, non-combustible, non-ozone depleting, non-toxic, low heat of vaporization, resistant to heat, stable composition, low surface tension, high density, low viscosity, low global warming potential (GWP), good material compatibility, and cost-effective.

Alternative cleaning options are: aqueous & semi-aqueous media, all class solvents - including non-ozone depleting chlorinated solvents, as well as "zero" alternative (no cleaning).

Alternative cleaning options in aqueous & semi-aqueous media

Aqueous alternatives are:

- ✓ Aqueous/saponifier: organic & inorganic
- ✓ Semi-aqueous: hydrocarbon base & terpene base
- ✓ Water-soluble organics: glycols & high molecular weight alcohols
- ✓ Water only



Advantages of aqueous cleaning processes

- World widely used
- Effective for various contamination types
- Flexible, widely applied
- Wide range of detergents available
- Suitable for high production
- Safe for operators

Disadvantages of aqueous cleaning processes

- Requires multi stage process
- Process monitoring is needed
- Wastewater must be treated
- Drying is a slow process with high energy consumption
- Corrosion to certain materials



Aqueous-cleaning machine- Automated in-line equipment



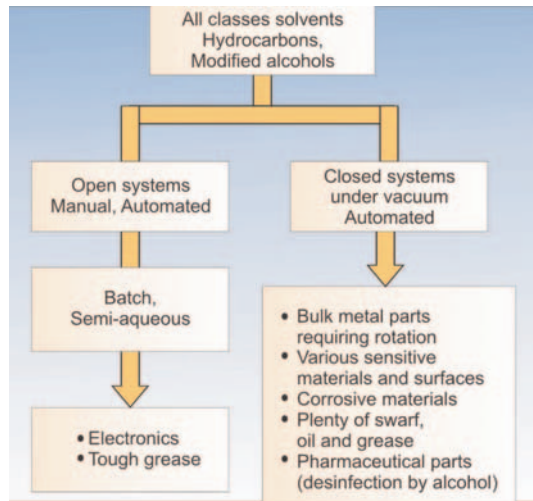
Aqueous-cleaning machine - unique enclosure

Alternative cleaning options with solvents

Alternative solvents are:

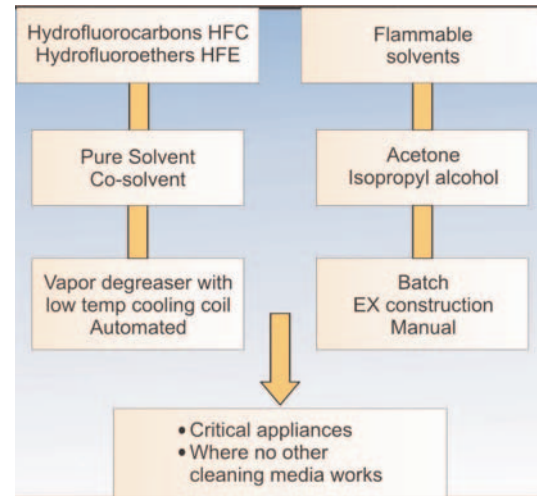
- ✓ Trichloroethylene & perchloroethylene
- ✓ HFCs
- ✓ Volatile methyl siloxanes
- ✓ Alcohol and cyclohexane/alcohol, esters, ketones

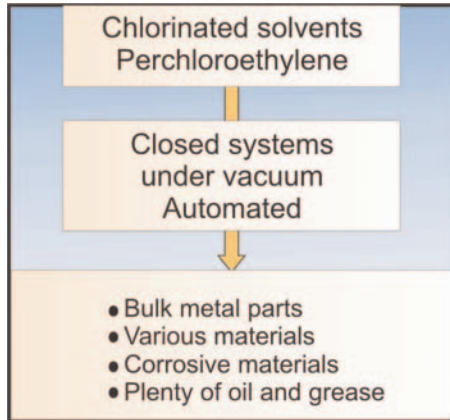
When to select all class solvents



- ✓ Amines. Amides
- ✓ High molecular weight alcohols
- ✓ Aliphatic/aromatic hydrocarbons
- ✓ n-Propyl bromide
- ✓ Sulphur derivatives: DMSO, DMSO2

When to select hydrofluorocarbons, hydrofluoroethers or flammable solvents





Advantages of aqueous with solvents

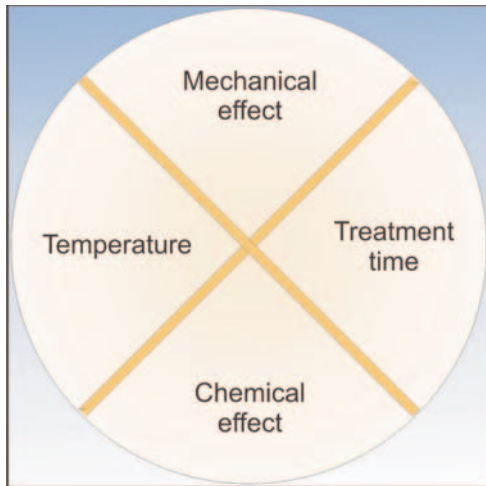
- Excellent degreasing capability
- Only one chemical is needed
- Solvent can be recycled by distillation
- Small space required
- Fast drying for many solvents
- No oxidation problems

Disadvantages of cleaning with solvents

- Not too efficient with soils and particles
- Inefficient to salts removal and oxidized surfaces
- Handling of toxic/flammable chemicals is needed
- Health and safety issues with traditional open-top equipment, closed systems are strongly recommended
- Reduced efficiency for single chamber cleaners
- Solvent removal implies operator exposure during recovery and final removal (incineration is recommended)

Factors with impact on the cleaning process

Modern cleaning technologies offer viable solutions to almost any cleaning specific issue without using environmentally hazardous chemicals. Efficient cleaning is always a result of several factors: Mechanical effect, Chemical effect, Temperature and Treatment time.



Mechanical effect

spray / water jets / rotating or tilting baskets a.s.o

Chemical effect

alkaline, neutral or acidic water based detergents / chlorinated solvents / various hydrocarbon solvents / modified alcohols / highly flammable solvents

Temperature

10°C increase in temperature will accelerate chemical reaction speed by 100%

Treatment time

increased treatment time cannot compensate shortcomings in other factors

Legislative Framework

- ✓ **Law nr. 84/1993** for the ratification of the Vienna Convention for the Protection of the Ozone Layer, adopted in 1995, of the Montreal Protocol on Substances that Deplete the Ozone Layer, adopted in 1987, and of the Amendment to the Montreal Protocol adopted at London, in 1990
- ✓ **Law no. 9/2001** for the approval of the Government Ordinance no. 24/2000 for the acceptance of the Amendment to the Montreal Protocol, adopted at Copenhagen in 1992
- ✓ **Law no. 150/2001** for the acceptance of the Amendment to the Montreal Protocol, adopted at Montreal, in 1997
- ✓ **Law no. 159/2000** for the approval of the **Government Ordinance no.89/1999** concerning the trade regime and the restrictions in using halogenated hydrocarbons that deplete the ozone layer
- ✓ **MWFEP Order no. 506/1996** for the approval of the export-import procedures for activities concerning substances, products and equipments listed in the Annexes of the Montreal Protocol
- ✓ **MWEP and MF Order no. 1112/2002** (National Customs Authority) concerning the nomination of the customs border offices for the import/export of the substances that deplete the ozone layer
- ✓ **Government Decision no. 58/2004** for the approval of the National Program for the phase-out of ODS
- ✓ **Starting with 2001**, Order of the Minister of Environment and Waters Management concerning the establishment of the contingent on ODS consumption and production is annually issued

Romanian legislation related to ODS was fully harmonized with the European Union legislation.

Restrictions on products that contain ODS and equipments and technologies based on ODS

In accordance with Law no. 159/2000 the use and trade of cleaning agents and solvents that contain one or more substances such as CFC and HCFC listed in the Annexes A, B and C of the Montreal Protocol are forbidden, excepting some cases:

- ✓ CTC use is allowed only:
 - as a solvent in chlorinating processes in closed system
 - as a solvent in processes where it can not be technologically replaced with another substance with a less ozone depleting potential.
- ✓ Laboratory applications - are permitted by the Montreal Protocol being considered as essential uses.
- ✓ Process agent - ODS use as process agent is a "solvent" application still permitted by the Montreal Protocol.

ODS management preventing air releases.

Staff Qualifications

In accordance with Law no. 159/2000:

- ✓ ODS air releases is forbidden.
- ✓ Recovery of ODS is compulsory during: maintenance, equipment dismantling, and following the process where these ones are used as cleaning agents.
- ✓ Mixing of different ODS during recovery / recycling / regenerating processes is forbidden.
- ✓ Maintenance of equipments containing ODS is allowed only to qualified and certified technicians.

Internet Sites

Ministries

Ministry of Environment and Water Management

<http://www.mappm.ro>

Ministry of Trade and Economy

<http://www.minind.ro>

Ministry of National Defense

<http://www.mapn.ro>

National Institute of Statistics

<http://www.insse.ro>

Customs National Authority

<http://www.customs.ro/vami/Main>

International Organizations / Institutions

United Nations Industrial Development Organization

<http://www.unido.org>

European Commission - ozone

[http://www.europa.eu.int/comm/
environment/ozone/](http://www.europa.eu.int/comm/environment/ozone/)

European Environment Agency

<http://www.eea.eu.int>

United Nations Environment Program

<http://www.teap.org>

Technical and Economics Advisory Panel

US Environmental Protection Agency

<http://www.epa.gov>

Conventions

United Nations Environment Program

<http://www.unep.org/ozone>

Vienna Convention and Montreal Protocol