

**MONTREAL PROTOCOL
ON SUBSTANCES THAT DEplete
THE OZONE LAYER**



UNEP

**2002 REPORT OF THE
SOLVENTS, COATINGS AND ADHESIVES
TECHNICAL OPTIONS COMMITTEE**

2002 Assessment

Montreal Protocol on Substances that Deplete the Ozone Layer

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UNEP
2002 REPORT OF THE
SOLVENTS, COATINGS AND ADHESIVES
TECHNICAL OPTIONS COMMITTEE

2002 ASSESSMENT

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ES. Executive Summary

Abstract

- The achievements of the Solvents, Coatings and Adhesives Technical Options Committee (STOC) over the past four years have consolidated its past work, while examining new developments in terms of replacement technologies, market evolutions, solvents toxicology etc. In particular, it has closely followed the problem regarding n-propyl bromide and has recommended the adoption of the precautionary principle, especially to reduce emissions and human exposure. It has also given particular attention to the specific needs of Article 5(1) countries. Almost total phase-out of the use of Annex A, Annex B and Annex C, Group III controlled solvents has now been achieved in non-Article 5(1) countries. There are still a few cases of users relying on stockpiled or recycled materials, but these stocks must be exhausted in the near future. A few Essential Use Exemptions have been granted, but these represent very small amounts. A recent study has shown unexpected 1,1,1-trichloroethane emissions in Europe, but it is thought that these may come from landfills where drums of used solvents may have been dumped many years ago. In addition, HCFC-141b is being rapidly phased out as a solvent in the European Union and the USA. The situation in Article 5(1) countries is very preoccupying because of few major solvents projects having been completed, except where subsidiary companies of large developed nation corporations have achieved in-house phase-out. Very few projects have been completed with small and medium users (SMUs) consuming less than 5 OD tonnes of solvents. There are many thousands of such users, consuming a major part of the remaining usage.
- There is much left to be achieved in the Solvents Sector. Effort is still required to help Article 5(1) solvents users, and especially the small and medium ones, to phase out the use of OD solvents. It is not yet clear how this can be effectively achieved. The STOC is monitoring how the China Solvents Country Project advances, but it is feared that this will not provide a complete solution for the SMUs. In particular, there is concern about the use of carbon tetrachloride (CTC), with a high ODP, for solvents applications by both large and small enterprises in some countries. A few important CTC projects are currently being handled by the MLF Implementing Agencies, but these represent only a fraction of the total consumption. One other obstacle that has been identified is illegal imports into, mostly, Article 5(1) countries that have already enacted restrictive legislation. These may represent a considerable proportion of baseline quantities, in some cases, and, of course, are not reported. This, and other factors, may mean that the total global OD solvents consumption is currently significantly higher than is reported.
- Future effort by the STOC must be targeted towards a rapid phase-out of the solvents, especially CTC and CFC-113. It is probable that only cutting the supply chain, as soon as possible, can do this. Delaying the cessation of production and imports of Annex A and Annex B solvents will involve greater

difficulty and larger costs than doing it now. This will inevitably cause hardship, especially for the many SMUs. The National Ozone Units (NOUs) will be forced to address this problem and the STOC is laying down an e-mail and Internet infrastructure that will allow NOUs to obtain detailed expert technical advice from its members, on request and free-of-charge, for rapid response in each sub-sector. This report is the first positive step towards this end because it has succinct, stand-alone, sub-sectorial chapters, for easy translation into local languages, each with e-mail addresses of experts for consultation. The STOC also needs to address the increasing use of Annex C solvents, especially HCFC-141b, in Article 5(1) countries; these are sometimes substituted for non-OD solvents. There are no technical barriers to a total and immediate phase-out of the use of OD solvents in nearly all applications. This includes CTC, CFC-113, 1,1,1-trichloroethane and HCFC-141b.

ES.1. Introduction

The 2002 report is considerably different from previous reports of the Solvents Technical Options Committee (STOC). The physical structure has been designed so that each sub-sector has a self-contained chapter that summarises new, essential, information and the technology choices available. It is intended that these individual chapters may be extracted for copying to interested parties, while remaining short enough for translation into local languages and subsequently distributed. To achieve this, the older technological details are not as complete as in previous editions. Readers requiring a more complete treatise are referred to the 1998 report.

Committee members have observed progress being made in phasing out ODSs throughout the world. While great progress has been made in developing countries, there have been some challenges in Article 5(1) countries, where the final phase-out will occur over the next few years.

There are no substantial technical barriers to phasing out ODSs. Alternatives are available that will meet the needs of all solvent users with very few exceptions.

There is still limited use of CFC-113 and 1,1,1-trichloroethane (methyl chloroform) in solvents applications in non-Article 5(1) countries; these are being met with stockpiled products and recycled material. Eventually, these will run out and alternatives will need to be implemented. Most enterprises in this situation have plans and will make the conversion once the supply of controlled materials is terminated.

The major obstacles in eliminating ODS use are in Article 5(1) countries and a separate chapter is devoted to this subject. The main barrier in overcoming such obstacles in these countries is communication and education of suitable alternatives.

The question as to what can be done to assist in the complete phase-out of ODSs in developing countries has been studied, resulting in the following remarks:

- Greater co-operation would be beneficial between the STOC and other international and national organisations, including within UNEP.
- Parties may wish to consider new measures to ease the financial burden of the numerous small and medium users (SMUs), which represent the majority of emissions in the sector.

Since the phase-out of the widely used CFCs and 1,1,1-trichloroethane in non-Article 5(1) countries, a number of new solvents that claim to be direct replacements have been marketed. The critical parameter for alternatives has been, and continues to be, that they should be non-ozone depleting. A notable exception is that of some hydrochlorofluorocarbons which possess small ozone-depletion values. These chemicals are Annex B Group 1 compounds and are scheduled to be phased out. Several promising alternatives have emerged from a review of historical data and by conducting new research. However, no single solvent or process was found to be a direct replacement for the CFCs and 1,1,1-trichloroethane. Hydrofluoroethers, hydrofluorocarbons, and hydrochlorofluorocarbons are among the organic solvents most widely used as substitutes. These materials have advantageous properties for many applications. Aqueous techniques are used in many cases. These are not the only acceptable alternatives. Descriptions of these and other alternatives are reported in this Assessment and in previous editions of the UNEP Solvents Technical Option Committee Assessment Reports. The potential user has the responsibility of evaluating and assessing an alternative as it applies to the specifics of the application.

Reference to n-propyl bromide (nPB) is limited. More details of this solvent are found in Appendix 1. Its use is not recommended at this time. New chemical solvents and processes are evaluated as they are marketed. However, a major break-through is rather unlikely in the near future.

ES.2. Sub-sectors

Each sub-sector, which may cover a range of applications, is treated in a separate chapter.

ES.2.1 Electronics Defluxing

Ozone-depleting solvents (ODSs) use in the electronics industry is a major source of emissions although the only significant use is in defluxing. This process removes the residues from the soldering operation to ensure maximum reliability and consistent performance. Several technologies may be used to achieve this but the selection is not always easy. The list of methods provides basic advice, but it is by no means exhaustive. Further details can be found in the 1998 and earlier Solvents Technical Options Committee Assessment Reports. In many cases, the advice in this chapter will be sufficient for enterprises to short list the technologies down to two or even one. From there, qualification testing will be required to select the most suitable materials, equipment, and processes. In most cases, it is possible to reduce production costs of the overall soldering and cleaning (if any) processes. This is therefore a candidate application to significantly reduce ODS emissions rapidly and effectively in many Article 5(1) countries.

ES.2.2 Precision Cleaning

Since the phase-out of the widely used CFCs and 1,1,1-trichloroethane in non-Article 5(1) countries, a number of new solvents that claim to be direct replacements have been marketed. Unfortunately, no single solvent or process was found to be a direct replacement for the CFCs and 1,1,1-trichloroethane. Hydrofluoroethers, hydrofluorocarbons and hydrochlorofluorocarbons are among the organic solvents most widely used as substitutes. These materials have advantageous properties for some applications. Aqueous techniques are used in some cases. New chemical

solvents and processes are evaluated when they are marketed. However, it is unlikely that a major breakthrough can be expected in the near future.

ES.2.3 Metal Cleaning

Metal cleaning is a surface preparation process that removes organic compounds such as oils and greases, particulate matter, and inorganic soils from metal surfaces. Metal cleaning prepares parts for subsequent operations such as further machining and fabrication, electroplating, painting, coating, inspection, assembly, packaging or further treatment such as heat treatment for surface modification. Parts may be cleaned several times during the manufacturing process. Almost all metal cleaning operations include solvent conservation and recovery practices and the use of alternative cleaning processes including alternative solvents and their blends contained solvent cleaning systems, low flash point solvents, co-solvent systems, aqueous cleaners, emulsion cleaners, mechanical cleaning, thermal vacuum de-oiling, liquid carbon dioxide, and no-clean alternatives.

Alternatives to CFC-113 and 1,1,1-trichloroethane must be selected and optimised for each application given the varying substrate materials, soils, cleanliness requirements, process specifications, and end uses encountered in metal cleaning. There is still a significant use of carbon tetrachloride in various cleaning processes in developing countries. These uses have been identified primarily where a low cost, non-flammable, and simple cleaning process is required, such as metal cleaning applications. While many alternatives seem obvious to improve worker exposure, total cost including environmental concerns, should be considered for any alternative.

Most of the CFC-113 and 1,1,1-trichloroethane used in metal cleaning applications can be replaced by existing alternatives in accordance with the Montreal Protocol. Developing countries should be able to closely follow the same scenario as the smaller companies in the developed countries. They may have an additional lag time in their own smaller industries. Each developing country will have somewhat different scenarios depending upon their unique industry structure, quantum of ODSs in use, and the selection of a suitable alternative.

ES.2.4 Dry Cleaning

The dry cleaning industry has been deploying ozone depleting solvents, CFC-113 and 1,1,1-trichloroethane, in specialised segments. CFC-113 was used primarily for delicate fabrics and those with sensitive dyes and trimmings. 1,1,1-trichloroethane was used mostly in the leather and suede applications in North America and, to a limited extent, for general dry cleaning elsewhere. It is believed that developed countries have completely phased out these solvents and switched over either to existing solvents, such as perchloroethylene, or to some of the new solvents mentioned in this report and its prior editions. There is no evidence to suggest that 1,1,1-trichloroethane was ever used in developing countries as a dry cleaning solvent, and very little, if any, CFC-113.

ES.2.5 Adhesives

While there is no drop-in replacement for 1,1,1-trichloroethane in adhesive bonding products, a variety of solvent-based and non-solvent adhesives provide high performance for specific applications. In many cases, changes to previous operating procedures must be made, but in general, these changes are not very restrictive.

Careful selection of available alternatives is important to adequately meet performance, cost, regulatory, and worker health criteria.

ES.2.6 Aerosols

HCFC-141b had emerged as a lead replacement candidate for CFC-113, CFC-11, and 1,1,1-trichloroethane since the non-Article 5(1) countries phase-out in 1996 in aerosol formulations as an active ingredient or as a solvent. However, HCFC-141b has an ozone-depletion potential about equal to that of 1,1,1-trichloroethane, therefore its use has been phased out in Europe since the beginning of 2002 and is scheduled in the United States at the end of 2002. The replacement solvents include petroleum distillates, water-based products, organic solvents, HFCs, and HFEs. Nevertheless, the use of HCFC-141b may continue in Article 5(1) countries until its scheduled phase-out date of 2040.

ES.2.7 Miscellaneous Uses

There are numerous miscellaneous industrial and laboratory applications that are not addressed in this report. Relatively small quantities of CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride are employed in most of these applications. In many cases, the alternatives are readily available but their selection and validation may require extensive effort. In other areas, some ODSs are still necessary, even though significant progress has been made towards a complete phase-out.

ES.3. Article 5(1) Countries

A review of the challenges that the phase-out of ODSs is facing in developing countries shows that suitable alternatives have to be chosen for CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride. HCFCs are the ODSs that need to be phased out in the future. Substitutes and alternatives have been identified throughout the world and are generally readily available for incorporation into existing processes. The major drawbacks to the implementation are access to information and knowledge about what are the acceptable alternatives and the economic and environmental considerations associated with them. Details of the alternative technologies are addressed in other chapters in this report dealing directly with the alternatives available for each application. Previous versions of the Solvents Technical Options Committee assessment reports also provide further information.

The major efforts to complete the transition away from ODSs in developing countries are dependent on the areas cited above, namely, 1) availability of information, 2) financial and economic needs to assist in the conversions, and 3) enforcement of current regulations.

ES.4. Appendices

Six appendices give additional useful information that is common to most of the applications. The first summarises the current situation regarding n-propyl bromide, with a recommendation of cautious use until there is clarification on the open questions of its effect on the ozone layer and its toxicity. Appendix 2 provides information on the proper use of halogenated solvents, particularly the non-ozone-depleting chlorinated solvents, based on known science, as well as policy decisions. Appendix 3 is an update on regulations introduced or proposed in Europe, Japan and the United States of America since the publication of the 1998 Assessment Report.

Appendix 4 tabulates the principal properties of typical ozone-depleting and non-ozone-depleting solvents. Appendix 5 gives a list of STOC Members. Appendix 6 is a Glossary that defines the most common technical terms used in this document.

1. Current Situation

1.1 Non-Article 5(1) Countries

All known production of Annex A and Annex B, as well as Annex C, Group III, controlled substances for solvents purposes has ceased in non-Article 5(1) countries, except as permitted under the provisions of the Montreal Protocol. However, some of these substances are still produced for feedstock and process agent uses.

Most users of these solvents, except where permitted under Essential Use Exemptions, have stopped employing them. It is probable that there are still a few users with remaining stockpiles or who are using recycled products. In the case of 1,1,1-trichloroethane and CFC-113 blends, material stockpiled since 1996 will have decomposed sufficiently as to make their use hazardous and less efficient, as well as endangering the quality of the equipment they are used in. On the other hand, pure CFC-113 has an indefinite shelf life if stored correctly.

As far as can be ascertained, illegal imports of OD solvents have diminished since 1998. This is very difficult to verify. It is very easy, for example, to relabel drums of 1,1,1-trichloroethane as being, for example, trichloroethylene. As the two substances are very similar in most properties, a casual inspection would not reveal the fraud; only a laboratory analysis could detect the difference. Some Article 5(1) country enterprises are still offering controlled substances for sale to non-Article 5(1) users by means of the Internet, e-mailing and other publicity. It is not known whether these offers have actually resulted in sales or, if so, how the products have been smuggled to the user.

A recent scientific report has indicated that unexpected quantities of 1,1,1-trichloroethane have been detected in the air, especially in Central Europe. These amount to an annual emission of about 2,000 OD tonnes. There is also a similar case with carbon tetrachloride, although with smaller, unspecified, quantities. The report considers that these emissions are inconsistent with either the use or illegal manufacture of the substances. The most plausible explanation is that they are emissions from landfills where drums, now rusting through, of used solvent have accumulated over many years, prior to the phase-out.

1.2 Article 5(1) Countries

It is very difficult to obtain accurate figures of the total manufacture, imports and use of OD solvents in Article 5(1) countries, despite the requirements for reporting. This is because:

- Some countries have not submitted reports or are late in doing so
- Some reports have been shown to be inaccurate, requiring modifications of the Country Plans
- The difficulty of identifying which solvents are ozone-depleting or not
- Complex commercial chains, often involving changing the labels to a trade name after blending
- Illegal imports.

This situation is generally improving, with the possible exception of carbon tetrachloride, which is very preoccupying because of its high ozone-depleting potential, its ease of manufacture, its high toxicity and a noted reluctance of users to change it for another, less toxic, non-ozone-depleting, solvent, on the grounds of increased cost. There are many users of very small quantities of carbon tetrachloride, for open-tank cold cleaning in some countries, involving thousands of OD tonnes of the substance.

The best estimates, based on data collected in 2000, for total manufacture and legal imports in Article 5(1) countries, are shown in Table 1.1. However, it is emphasised that these are estimates and not precise figures.

Table 1.1 Estimated global solvent use in Article 5(1) countries

	Physical tonnes	OD tonnes
Carbon tetrachloride*	14,000	15,400
CFC-113	7,800	6,240
1,1,1-trichloroethane	24,000	2,400
	Total	24,040

Note

* The figures for carbon tetrachloride include process agent, but not feedstock, use, because it is not easy to separate these in some countries. It is possible that process agent use may amount to somewhere between 5,000 and 6,000 physical tonnes.

1.3 Multilateral Fund supported projects

As at early 2002, the Multilateral Fund had completed about 50 Solvents Projects, to the stage of a published Project Completion Report. This does not compare favourably with other sectors, either in terms of the number or the grants disbursed. There are many reasons for this anomaly (see Chapter 9) but it is acknowledged that this sector is the most difficult to implement. In particular, the majority of solvents users consume less than 5 OD tonnes of solvent per year, making it almost impossible to be cost-effective, while offering traditional aid through the Implementing Agencies.

One project in the course of implementation is the China Solvents Country Plan. The results from this are eagerly awaited, as other large consuming countries, with appropriate modifications, may usefully copy the principle. In particular, the manner in which small and medium users are able to phase out OD solvents will be interesting.

In addition, some bilateral projects have been very useful. One such has been between France and Malaysia, where “hands-on” technology transfer of “no-clean” flux and solder paste use has been offered to many small and medium enterprises, involving significant quantities of CFC-113. Similar approaches are to be encouraged, but experience has shown that it is insufficient to tell users how it can be done, such as with seminars or even demonstrations, but the experts have to physically show the beneficiaries how to do it and to trouble-shoot any problems encountered. The corollary is that the experts need to spend considerable time in the beneficiary

country, which may be counter-productive to their employers' needs, if they come from industry.

1.4 The role of STOC over the past four years

The STOC has accomplished considerable work, under difficulties. Two of the achievements have involved very controversial subjects. A number of the members were nominated to the TEAP Task Force on n-propyl bromide, co-chaired by two STOC members. This involved a monumental study of many hundred man-hours, a report on which was published in the April 2001 TEAP Report. The current situation on this topic is in Appendix 1 of this present Report.

The second one results from two STOC members having been commissioned by the Multilateral Fund Secretariat to conduct a mid-term technical evaluation of completed Solvents Sector projects in seven Article 5(1) countries. Apart from the fact that this project has provided the STOC with much new general information about the problems that solvents users experience in practice, the MLFS consequently asked TEAP and, thus the STOC, to give recommendations on how to safely and economically use halogenated solvents with minimum environmental damage. This resulted in the document in Appendix 2 of this present Report. This subject is particularly controversial as there are contradictions between the national regulations of different countries and the interpretation of known scientific data.

The STOC members have closely followed the evolution of the marketplace and new products. In particular, new hydrofluorocarbon and similar solvents and blends have appeared. Some of these, with higher chlorocarbon content, are cheaper, more effective and have a lower GWP; this is an encouraging sign. HCFC-141b is being phased out in Europe and the USA, but this does not appear to have caused undue difficulties. HCFC-225 is now available in blends with a lower toxicity because of better isomer separation.

1.5 The future role of the STOC

The role of the STOC has changed over the last four years and is continuing to change. Whereas, in the past, the need to help large users to find the right technology for a given application has been paramount, this is now secondary to the needs of the small users in Article 5(1) countries. This change has been difficult to assimilate, but it has not been made easier by the combination of reduced funding available for many non-Article 5(1) country members and travel restrictions imposed by some employers following the terrorist activity in the USA and elsewhere. TEAP, the co-chairs of STOC and the members are currently consolidating this change with a view to having a team that is able to be effective in meeting the needs of helping Article 5(1) countries to eliminate the use of the remaining 24,000 OD tonnes of solvents as quickly as possible. It is emphasised that there are no technical barriers to achieving this, even tomorrow; it can be done. The real barriers are the way to proceed without causing undue hardship and the psychological resistance to change.

To do this, the STOC must be approachable by those needing help, at any level, including by the National Ozone Units and others. This may mean closer co-operation

with other organs within the Montreal Protocol framework and this is seen as a major part of the future role of the STOC.

2. Electronics defluxing

Summary

ODS use in the electronics industry is a major source of emissions. The only significant use is in defluxing. This process removes residue from the soldering operation, to ensure maximum reliability and preserve performance. Several technologies may be used to achieve this but the choice is not always easy. A list of methods gives basic advice, without being an exhaustive treatise. Further details are given in the 1998 and earlier STOC assessment reports. In many cases, this advice will be sufficient for enterprises to shortlist the technologies down to two or even one. From there, qualification testing will be required to select the most suitable materials, equipment, and processes.

In most cases, it is possible to reduce production costs of the overall soldering and cleaning (if any) processes. This is therefore a candidate application to significantly reduce ODS emissions rapidly and effectively in many Article 5(1) countries.

2.1 Introduction

The electronics industry has been using 1,1,1-trichloroethane and, above all, CFC-113 blends for defluxing for many decades. This has been the single biggest cause of ozone depleting emissions in the solvents sector, probably accounting for over 60 per cent of the total.

Defluxing consists of removing the residue remaining after soldering the components onto a planar substrate, most commonly a printed circuit board. The soldering process uses a flux to ensure the chemical and metallurgical bond between the solder and the conductors of the board and the component. Fluxes used in electronics are generally mild organic acids of different compositions, to suit the chosen process. In some cases, these acids are either so mild or are imprisoned in a matrix that they can cause no harm and may be left on the assembly. In other cases, noted below, the flux residues must be removed.

- For high-reliability hardware;
- Where the assembly is subjected to poor climatic operating conditions or dust;
- Where the assembly must have a protective (conformal or potted) coating;
- Where the circuit operates at high voltage gradients or currents;
- Where the circuit runs at a high bit rate or frequency;
- Where a good aesthetic appearance is essential;
- Where the customer specifies it (whether it is technically necessary or not);
- In some cases, with very high density circuits;

In non-Article 5(1) countries, conversion to alternatives has been quasi-total for many years. Some countries had almost total phase-out in this sub-sector since about 1993. The biggest obstacle to phase-out was not the lack of substitute materials and processes so much as choosing the most suitable one for a given application. This was also sometimes delayed by the time required to change manufacturing specifications, some of which were firmly entrenched in the mores of the industry, especially in the military field. This has now been resolved in non-Article 5(1) countries, but not in all Article 5(1) countries.

In Article 5(1) countries, similar problems, and a few additional ones, exist. This leads to a somewhat unnecessary slowdown in phasing out these substances. It should be pointed out that, prior to the Montreal Protocol, it is estimated that approximately 18 per cent of total ozone-depleting emissions was due to the solvents sector and 60 per cent of this a result of defluxing, making an aggregate of over 10 per cent. It is possible that this percentage is higher today because some sectors such as refrigeration and foam blowing have been able to achieve a proportionally higher phase-out rate due to Multilateral Fund aid.

It must be realised that electronics manufacturing is mostly made up of a large number of very small fabrication units, each with very low ODS consumption. Even large companies frequently sub-contract their production to small subsidiaries or contractors. For example, in a small country like Switzerland, in 1990 there were an estimated 3,000 companies assembling electronics circuits, each a potential ODS user. There are certainly tens of thousands of companies using CFC-113 or 1,1,1-trichloroethane today. Some of these may be unaware that their cleaning product is ozone-depleting because it is often blended locally and sold under a trade name.

2.2 Statement of Sub-sectorial Problems

The following problems have been identified, especially in respect to Article 5(1) countries:

- Lack of practical knowledge and information of different flux types.
- Lack of availability, in some countries, of locally produced flux types and cleaning technologies.
- Understanding that the soldering process and associated quality control may need to change.
- Majority of users are SMUs, which have difficulties accessing government and Multilateral Fund resources.
- Small cleaning gaps with modern chip-scale packages, including micro-BGAs.

In many cases, these problems have resulted in:

- Delays in phasing out ODSs, especially CFC-113;
- When changes have been made, results have often been less than satisfactory, with significantly increased production costs, where savings were possible;
- Quality not consistent with product requirements (may be insufficient, or too good and consequently too expensive).

2.3 Alternative Technology Considerations

The selection of the alternative should be based on the following five primary factors.

- Should not be an ODS.
- Should enable the enterprise to maintain a product reliability level at least equal to previous methods.
- Should be economical.
- Should not create significant environmental impact.
- Should not compromise worker or consumer health and safety.

The following hierarchy of alternative classes (in order of most preferred first) has been assembled in consideration of these five primary factors to assist enterprises with their decision:

1. “No-clean” fluxing, without subsequent cleaning.
2. Water-soluble chemistry, followed by a straight water wash process.
3. Rosin or similar fluxes, followed by saponification and a water wash process.
4. Rosin or similar fluxes, followed by hydrocarbon/surfactant (HCS, “semi-aqueous”) cleaning and a water wash process.
5. Hydrocarbon cleaning.
6. Halocarbon cleaning.

2.3.1. “No-clean” Technology

Wherever possible, this is the first choice. In developed countries, this alternative represents approximately 80 per cent of total flux and paste sales. It is an excellent compromise for most applications, except where a long product lifetime with ultra-high reliability is required, because it needs no cleaning materials or process. Major disadvantages include a narrower operating window for soldering (requiring good training and process control), and it may result in a small increase in faulty solder joints (requiring manual retouching). In developed countries, this method is used for the majority of electronics manufacturing, even possibly military hardware (with extremely good process qualification and control).

It should be noted that not all “no-clean” soldering fluxes and pastes give the same results. As a rule of thumb, those that solder easily with few defects are those where the end-product reliability is lowest and *vice versa*.

Great care should be taken if it is proposed to use a “no-clean” flux or paste where cleaning or conformal coating is necessary, since these fluxes are generally not formulated to permit this. Nevertheless, a few users do this but only after extensive material selection and process qualification.

2.3.2. Water-soluble Technology

This is the method of first choice where cleaning is required for any reason. It is the most frequently employed technology in non-Article 5(1) countries when assemblies are cleaned. Similar to “no-clean” technology, it is also a compromise, but the trade-off here is that it requires a well controlled cleaning process. It requires a specially formulated flux that usually allows very easy soldering, even of oxidised surfaces. In the case of the recently popularised electroless nickel and gold finish, aged circuits may be difficult to solder with any flux except these ones.

The cleaning process is critical and machines are available for all volumes of production. However, caution is advised in machine selection. It is essential to conduct practical trials to ensure that the cleanliness and drying qualities are sufficient to meet the real needs, before choosing any particular make or type of equipment. Some low-cost equipment, either conveyerised or batch, may not give satisfactory results.

Drying is also critical and should consist of a gross mechanical removal of excess water and the residual contamination, by centrifugation, air knives or even violent shaking, followed by a final stage of evaporative drying. Some low-cost equipment

may dry only by evaporation, however this allows the residual contamination to remain on the assemblies and is very energy-intensive, causing potential indirect “global warming” in the electricity generating stations.

Some equipment is available from Article 5(1) manufacturers.

2.3.3. Saponification Technology

Saponification is the conversion of an insoluble rosin, or similar, flux or paste into a soluble soap. The process consists of this chemical conversion followed by a water wash, as described previously for water-soluble technology. The chemical process is not always easy, especially where there are thick flux deposits. The correct choice of the combination of flux and saponifier is essential. Since the 1998 STOC assessment report was written, a new family of saponifiers, giving better performance, has become popular. These are slightly less aggressive than conventional saponifiers, but require new filtering constraints. This means that not all aqueous cleaning machines are suitable for the process. In a few cases, specific “no-clean” fluxes have been satisfactorily cleaned with these new saponifiers, which have a higher purchasing cost but a longer working life.

All saponifiers are corrosively alkaline and ionic. Therefore the water wash and rinse phases must be perfect to ensure high reliability, if this is necessary. They also require taking considerable health, safety, and environmental precautions (see below).

2.3.4. Hydrocarbon/Surfactant Technology

This method uses a water-soluble or water solubilised, low-volatility hydrocarbon solvent to dissolve a rosin or similar flux. The solvent, with dissolved contaminants, is then washed off with water and rinsed, as described previously for water-soluble technology.

This technology was initially popular in developed countries because it did not require a change in flux type, but is comparatively less in use today because it is a costly process as compared to water-soluble technology. However, it gave excellent results in terms of the attainable cleaning quality, in well-regulated processes.

2.3.5. Hydrocarbon Technology

Straight hydrocarbon cleaning is rarely used today. All the products are flammable or combustible. The flammable ones, such as undiluted or blended isopropanol, present a risk that is unacceptable for most applications and are frequently very poor in cleaning quality, because not all the thermally modified flux residues and organic metallic salts formed after soldering are soluble in these products.

Some of the combustible blends are better for cleaning quality but present the problem of being difficult to dry. They frequently require 4 to 10 times the energy to evaporate than does water, in addition to long drying times.

Furthermore, all these solvents are mild greenhouse gases but strong VOCs.

The STOC considers that hydrocarbon technology cannot be recommended for defluxing, except under extraordinary and well-defined conditions.

2.3.6. Halocarbon Technology

Halocarbons have been used traditionally for defluxing, ever since printed circuits and other planar interconnection methods were developed. Their advantages of low toxicity and good plastics compatibility (CFC-113) were paramount.

It would seem obvious that this technology would remain a logical choice; however no suitable “drop-in” replacement is available. HCFC-141b and HCFC-225 blends are being used. Both these substances are controlled under the Montreal Protocol and scheduled for phase-out.

As a rule, the chlorinated solvents are too aggressive for printed circuits but may be usable with hybrid circuits on condition that the components are compatible.

HFC and HFE blends are also used for some particular niche applications, but their performance, requiring long and complex cycles for effective total defluxing, is such that their price rules them out as suitable candidates for all but the most exceptional application.

n-Propyl bromide is a potential candidate but is not recommended because of its unknown ozone-depleting potential and toxicity, at the time of writing (see Appendix 1).

All halocarbon defluxing requires low-emission machines designed specifically for the application, usually very modern open-top vapour degreasers. Older (prior to 1990) machines can rarely be economically modified or retrofitted to use these solvents. Solvent emissions may be drastically reduced with correct operator training, machine design, handling procedures, and recycling.

2.4 Environmental, Health, and Safety (EHS) Constraints

Fluxes of all types used for electronics offer little problem in terms of EHS. Most of them are based on light alcohols as a carrier solvent but recent developments have produced some so-called “no-VOC” types, using water, with or without surfactants, as a carrier. In fact, the organic activators and vehicles are heated to typically 250°C during the process and largely evaporate, releasing VOCs. The non-solvent components of the fluxes are generally fairly benign, composed largely of products found in nature, such as rosin or other resins, fruit or similar carboxylic acids, amino acids in meat proteins, and hydrochlorides of amines and amino acids.

Water cleaning, whether in a straight water-soluble, saponifier or HCS process, does require careful examination. SMUs will not be able to use a closed-circuit recycling system; the corollary of this is that waste water is discharged to drain. In some cases, this is possible, but it is necessary to ensure that local regulations regarding metal cation content, pH and COD₅/BOD₅ are met. It is usually possible to find ways of economically handling these problems if they arise, but this may require expert help.

For larger enterprises, it may be economical to recycle the waste water for re-use. Experience has shown that it would be optimistic to obtain more than 75 to 80 per cent recycling efficiency, so that the shortfall must be made up from incoming fresh water. The losses are due to evaporation, drag-out, and solubilising waste streams. The latter would require disposal as hazardous waste, since they will contain the flux residues, including heavy metal salts, column regeneration liquors, and so on.

Saponifiers are hazardous. Most of them contain monoethanolamine (MEA), which is a toxic substance, often volatilised in the process. Operator exposure limits must be respected in the workplace. In all cases, saponifiers are strongly alkaline (pH 10.5 – 14) and this presents a definite and distinct operator hazard, requiring careful protection and training. Used saponifier baths are hazardous waste, containing a strongly alkaline mixture of flux residues, heavy metal salts, chelating agents, etc. If treatment by competent chemists within the enterprise cannot meet all waste water discharge regulations, then it must be shipped to a nationally recognised waste chemicals disposal plant.

HCS solvents are frequently combustible, presenting a minor fire hazard. They are rarely very toxic, but the manufacturer's MSDS and instructions must be followed. Drag-out of the solvent in the wash water may, in some cases, present a problem for discharge to drain. They may contain unacceptable levels of heavy metal salts or the BOD₅ may be too high. Either of these possibilities may upset the functioning of sewage treatment plants, creating a potential health hazard. Storage and use areas of these products must be contained to reduce the risk of ground water contamination in case of an accidental leak. It must be noted that concrete affords no protection because it is porous. HCS solvents are also VOCs.

Hydrocarbon solvents may present a higher fire risk and all storage and use areas must be totally flameproof and protected according to local regulations, as well as protected against accidental leaks as previously mentioned. The solvents themselves are usually innocuous, but the manufacturer's MSDS and instructions must be followed. Hydrocarbon solvents are also VOCs.

Halocarbons are all more or less toxic and the appropriate precautions must be taken for both storage and use areas. Accidental leaks may be especially dangerous as penetration through concrete, soil, road surfaces, etc. is very rapid, and protection is essential. A small quantity reaching a water table may render the water unfit for consumption for many years. Operator protection is also essential due to the high vapour toxicity of many halocarbon solvents. The correct choice of low-emission machines installed in well designed plants will help in this respect. Halocarbons are VOCs and many of them have moderately high GWPs.

2.5 Other Relevant Information

A new problem is coming to light—there is an international trend towards eliminating the lead in solder used in electronics assembly. The downside as far as defluxing is concerned is that the residues from soldering with some lead-free alloys are more difficult to clean. This may accelerate the trend towards “no-clean” soldering (although this has proved to be more difficult). However, where cleaning is necessary, it may be mandatory to change the cleaning process or at least the process times in order to achieve satisfactory results. Furthermore, although there will be no lead in the cleaning solvents or water, there will be an increase of tin, copper, and silver salts in compensation. In particular, silver salts have been shown to be environmentally undesirable because of their mobility in soil and their danger to aquatic life and the bacterial action of sewage treatment processes. Companies going lead-free should pay particular attention to their waste disposal.

The design of printed circuit boards is often critical for soldering or cleaning efficiency and should be taken into account as a component of the concurrent engineering process.

Modern chip-scale packages, including micro-BGAs, are manufactured with a high density of interconnections and very small clearances between the component and the substrate. This leads to a paradox that, when cleaning is essential, it is almost impossible because of the small clearances. This problem has not been adequately resolved and work is still in progress to find a reliable solution.

2.6 Conclusion

The technologies necessary to achieve a 100 per cent phase-out of ODS exist, for enterprises of all sizes. The slowness that has been evident for this to take place is due to a number of factors. Defluxing remains as one of the most important single sub-sectors still contributing to ozone depletion. NOUs may wish to consider the advisability of contributing to a significant and rapid improvement in emissions by helping their national electronics industry. At the same time, in most cases, the overall production costs can be reduced.

2.7 Sources of Additional Relevant Information

Sources of further information on alternative cleaning solvents and alternate cleaning technologies as well as application guidelines can be found in four recently updated cleaning handbooks issued by IPC at

<http://www.ipc.org/>:

- IPC-SC-60A Solvent Cleaning
- IPC-SA-61A Semi-Aqueous Cleaning
- IPC-AC-62A Aqueous Cleaning
- IPC-CH-65A Cleaning Handbook

<http://www.protonique.com/com/files/clean.htm>

<http://www.protonique.com/unepstoc> (the 1998 electronics chapter may be found here)

e-mail addresses of STOC members who can offer advice:

- b_ellis@protonique.com
- prollet@promosol.com
- wgkenyon1@aol.com
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3. Precision Cleaning

Summary

Since the phase-out of the widely used CFCs and 1,1,1-trichloroethane in non-Article 5(1) countries, a number of new solvents that claim to be direct replacements have been marketed. The critical parameter has and continues to be that they be non-ozone depleting. A notable exception is that of some hydrochlorofluorocarbons which possess small ozone-depletion values. These chemicals are Annex B Group 1 compounds and are scheduled to be phased out.

Several promising alternatives emerged from a historical database and new research was conducted. Unfortunately, no single solvent or process was found to be a direct replacement for the CFCs and 1,1,1-trichloroethane.

Hydrofluoroethers, hydrofluorocarbons and hydrochlorofluorocarbons are among the organic solvents most widely used as substitutes. These materials have advantageous properties for some applications. Aqueous techniques are used in some cases.

These are not the only acceptable alternatives. Descriptions of these and other alternatives are reported in this chapter and in previous editions of the UNEP Solvents Technical Option Committee Assessment Reports. The potential user has the responsibility of evaluating and assessing an alternative as it applies to the specifics of the application. Reference to n-propyl bromide (nPB) is limited. More details of this solvent are found in Appendix 1. Its use is not recommended.

New chemical solvents and processes are evaluated when they are marketed. However, it is unlikely that a major breakthrough can be expected in the near future.

3.1 Introduction

Precision cleaning applications are characterised by the high level of cleanliness required to maintain low-clearance or high-reliability components in working order. They are used in a variety of manufacturing industries, such as aerospace, microelectronics, automotive, optical and medical. The primary factor that defines the applications where a precision cleaning process is required is high standards for the removal of particulate matter or organic residue.

There are many types of contaminants that may need to be removed in a precision cleaning process. These contaminants are generally divided into either particulate contamination or non-particulate contamination. Particulate contamination is the type of contamination usually resulting from a preceding manufacturing process, such as cutting, drilling, grinding or buffing of component parts. Non-particulate contamination is usually composed of organic residue, such as machining oils, waxes, fingerprint oil etc.

A number of companies have successfully tested and are currently using CFC-113 and 1,1,1-trichloroethane alternatives to clean precision instruments. Companies are also implementing conservation and recovery practices to reduce solvent use in the short-

term. Possible alternatives include solvent and non-solvent options. Solvent options include aqueous and hydrocarbon-surfactant (semi-aqueous), alcohols, synthetic aliphatic hydrocarbons, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) and their blends, and other miscellaneous solvents. Non-solvent options include supercritical fluid cleaning, UV/Ozone cleaning, pressurised gases, and plasma cleaning. Although testing still needs to be done for specific applications, alternatives are available for CFC-113 and 1,1,1-trichloroethane in virtually all precision cleaning applications.

3.2 Statement of Sub-sectorial Problems

The implementation of precision cleaning alternative solvents and processes in non-Article 5 countries has posed many problems. Some alternative solvents and processes are expensive, which can be a restriction. For example, where CFC-113 was relatively low-cost, emerging alternatives can be up to 10 times more expensive. However, recovery of used solvents and subsequent purification can reduce the operational costs, although purification equipment and implementation can be expensive. This may result in the use of less acceptable materials for the environment and health and safety.

It is clear that the implementation of alternatives may place a financial burden on users. However, considering that some of the alternatives can be used with confidence both from the standpoint of reliability and environmental impact it is worth the relatively high incremental capital cost.

Many Article 5(1) countries continue to use ODSs because of their later phase-out date. However, once the staged phase-out restricts supplies, this may become a serious problem. In addition, stockpiled supplies will eventually be depleted.

3.3 Suitable Options -- Materials and Equipment

Recommendation of a hierarchical list of suitable alternatives in order of suitability is impractical and even unwise, as individual cases and requirements are unique. Therefore the following list is compiled with no intention of ranking and is by no means a complete listing of potential alternatives. For precision cleaning, the use of solvents is, however, recommended over multiple steps processes, in many cases.

- Hydrochlorofluorocarbons (HCFCs)
- Hydrofluoroethers (HFEs)
- Hydrofluorocarbons (HFCs)
- Chlorinated and other miscellaneous solvents
- Alcohols and ketones
- Aliphatic hydrocarbons
- Aqueous cleaning
- Hydrocarbon-surfactant (semi-aqueous) cleaning
- Supercritical Fluids

3.3.1. Hydrochlorofluorocarbons (HCFCs)

HCFCs are transitional alternatives since their ozone-depletion potential (ODP) values, though small, are not zero. As a result, they are subject to a 99.5% phase-out

by the year 2020 in non-Article 5 countries, through staged reductions. Nevertheless, they have the excellent physical properties of CFCs, such as low surface tension and non-flammability. Some of them can be used in certain applications with minimal or no process changes.

Several HCFCs (e.g., HCFC-225ca/cb and HCFC-225G) have been proposed as possible CFC-113 and 1,1,1-trichloroethane substitutes. Appendix 4 shows the physical properties of some of these chemicals and compares them with CFC-113 and 1,1,1-trichloroethane. HCFCs usually can be incorporated with little or no additional capital expenditure, provided that emissions are already minimal.

A significant advance with regard to HCFC-225 has been achieved since the UNEP STOC Report 1998. HCFC-225 is a blend of the ca/cb isomers that presented concern with the presence of the ca isomer. Technology advances have allowed the separation of the ca/cb isomers. This resulted in obtaining near-pure, less toxic cb isomer. This is a significant development and makes its use easier.

3.3.2. Hydrofluoroethers

Numerous studies have shown that fluorinated compounds containing an ether linkage can result in shorter atmospheric lifetimes as compared to many of the CFC replacements currently being developed.

Two HFEs (HFE-449s1 and HFE-539sf2) are non-flammable, non-ozone depleting, low in toxicity and possess some physical and chemical properties similar to CFC-113. HFEs have successfully replaced CFCs, HCFCs, HFCs and PFCs in certain precision cleaning operations, aerosols and carrier fluids, as well as in some niche industrial solvent applications. HFEs can be used in many of the applications typically employing HFC or PFC liquids, leading to significant reductions in greenhouse gas emissions, depending upon the compounds involved in the substitution.

Pure HFEs can be used successfully in certain applications. However, the solvency power of pure HFEs is much lower than that of CFC-113, 1,1,1-trichloroethane or the HCFCs. To accomplish more difficult cleaning applications, blends and azeotropes of HFEs with organic solvents can be used. These mixtures provide significantly increased solvency and lower cost on a per kg basis as compared with pure HFEs. Mixtures of HFE-449s1 and HFE-569sf2 are available with solvents such as ethanol, isopropanol and trans-1,2-dichloroethylene.

3.3.3. Hydrofluorocarbons (HFCs)

Hydrofluorocarbons (HFCs) have been introduced as a replacement for CFC-113 since its phase-out. The neat HFCs and their azeotropes and/or blends have zero ODP and medium GWPs, as well as many desirable properties similar to CFC-113 such as low toxicity, good compatibility, excellent chemical and thermal stability, non-flammability and selective solvency for the applications. Two HFC solvents currently commercially available are HFC-43-10mee and HFC-365mfc. Several manufacturers are working on other replacement HFCs

HFC-43-10mee is non-flammable under all conditions; however, HFC-365mfc has a flash point and flammable range and must contain an inerting material such as HFC-43-10mee or HFE-449s1 to be totally non-flammable.

HFC-43-10 and its formulations have been successfully replacing ODSs in defluxing, precision cleaning, displacement drying and some other niche applications. It is also successfully replacing high GWP perfluorocarbons (C_5F_5 , C_6F_6 and C_7F_7) in computer disk drive coating and cleaning applications and some select electrical and heat transfer applications.

3.3.4. Chlorinated Solvents

Chlorinated solvents, such as trichloroethylene, perchloroethylene and methylene chloride are available in high-purity, as well as commercial grades. They have been successfully applied in many precision cleaning applications, especially as a substitute for 1,1,1-trichloroethane. However, they may be considered unsuitable for bench-top cleaning in clean room conditions, because of the difficulty in extracting toxic vapours from the operators' environment. On the other hand, they may be suitable for vapour degreasing in appropriate equipment.

3.3.5. Alcohols and Ketones

Common organic solvents are alcohols such as ethanol, isopropanol, several glycol ethers (methyl, n-butyl, and diethyl) and ketones, such as acetone, MEK etc. Most of these solvents are chosen for their high polarity and for their very effective solvency. These substances are flammable and care must be exercised. Some of these materials are also used for precision wipe cleaning.

3.3.6. Aliphatic Hydrocarbons

Aliphatic hydrocarbons, formulated for tighter control on composition, odour, boiling range, evaporation rate etc., may be employed in some precision cleaning processes.

3.3.7. Aqueous Cleaning

Aqueous cleaners use water as the primary solvent. Synthetic detergents and surfactants are combined with special additives such as builders, pH buffers, inhibitors, saponifiers, emulsifiers, deflocculants, complexing or chelating agents, antifoaming agents, and others. They provide multiple options in formulation blending, such as the use of corrosion inhibitors and pH buffers.

The key stages of an aqueous cleaning process are washing, rinsing, drying, water treatment, and waste recycling/disposal. Each of these steps is important and an integral part of the aqueous cleaning system.

Recent advances in aqueous cleaning technologies have extended their use in industry. Improvements in ultrasonic equipment, membrane filtration and aqueous cleaner technologies have enabled the use of aqueous cleaning for even some of the most demanding precision cleaning applications. Closed loop aqueous cleaning has gained wider acceptance in the past few years, as users have experienced greater cleaning efficiencies and reduced life cycle costs for applications in the aerospace, medical, optical and semiconductor industries. While the initial cost of equipment is still high, cost is mitigated over the life cycle by recycling products.

Improvements in mechanical assist technologies are key to obtaining efficiencies needed for precision cleaning applications. Mechanical agitation contributed 80 – 90% to the overall efficiency of aqueous cleaning.

A new generation of recyclable cleaners contain surfactant technologies that allow near-neutral pH chemistries that are low foaming in spray wash applications, yet efficient in a wide range of immersion, spray wash and ultrasonic equipment. These cleaners are compatible with micro- and ultra-filtration membranes and are thus well suited to provide extended bath lives for precision cleaning requirements.

Finally, while the technologies described above work effectively to precision clean sensitive hardware, organic solvents may be necessary for final non-volatile residue determinations.

3.3.8. Hydrocarbon-surfactant (Semi-aqueous) Cleaning and co-solvent cleaning

Hydrocarbon-surfactant cleaning consists of an initial organic solvent process using a low vapour-pressure solvent followed by a water wash and rinse. Alternatively, the hydrocarbon solvent step may be followed by a rinsing step in a halocarbon solvent.

3.3.9. Supercritical Fluids

Supercritical fluids (SCF) are chemicals that are normally liquid or gaseous at standard temperature and pressure. However, when the pressure and temperature are increased to specific levels, the chemical reaches a supercritical state and exhibits enhanced solvent properties. This is a niche application because of its high cost and technical complexity.

Details of supercritical fluid cleaning can be found in UNEP STOC Report 1998.

3.4 Environmental, Health and Safety Constraints

Two major factors in determining the feasibility of any proposed alternative to CFC-113, 1,1,1-trichloroethane and other ODSs are the environmental impacts and the energy requirements of the substitute. The wide variety of alternatives processes available carry with them an equally wide variety of environmental and energy considerations.

Conservation and recovery procedures have proven to be effective in reducing the environmental impacts of industrial solvent usage. These procedures are extremely valuable, not only in cases where acceptable alternatives to CFC-113 and 1,1,1-trichloroethane have not yet been found, but also where organic solvents used in the system vaporise. Currently, though solvents can be recycled, the recycled solvent is rarely used in precision cleaning applications due to perceived impurities. The solution to this problem is the individual recovery and handling of any solvents in use at a given location. Careful handling will help prevent the mixing of solvents, thereby allowing for treatment and potential reuse. Additionally, companies may purchase small, inexpensive, solvent reclamation equipment to offset the high costs of solvent disposal.

Several of the alternatives require waste water treatment. These alternatives are the aqueous and hydrocarbon solvent (HCS) cleaning processes. In both cases, the treatment of waste water can often be performed in-house so that the water may be recycled.

The ozone-depletion potential (ODP) associated with processes is an important environmental consideration. HCFC solvents have small ODPs, which may limit their use. Conversely, the ODP of zero associated with HFCs and HFEs make them attractive. Some new solvents have appeared on the market since 1994 with small, but significant, ODPs, namely chlorobromomethane, now a controlled substance in Annex C, Group III, and n-propyl bromide. Since the latter solvent is not yet controlled under the Montreal Protocol, it has been very aggressively marketed (see Appendix 1).

Another important consideration of alternatives to CFC-113 and 1,1,1-trichloroethane in precision cleaning applications is the possible health effect on workers and the general population. Each alternative has occupational hazards associated with its use. For example, aliphatic hydrocarbons are flammable, most organic solvents are VOCs, some gases are asphyxiants, most fluorocarbon solvent vapours are very strong “greenhouse gases” and chlorinated solvents are toxic.

While energy considerations are also important in the choice of an alternative precision cleaning method, they usually fall behind other environmental impacts in their importance. High-energy consumption will obviously increase the operating costs, as well as increase greenhouse gas emissions in fossil-fuel fired power stations. Depending on the cost of energy in different parts of the world, this could be the deciding factor in selecting an alternative. Organic solvents may require less energy than multiple step alternatives such as aqueous or semi-aqueous systems. Other methods, such as the supercritical fluids, can be expensive.

Further health considerations regarding alternatives are being evaluated continually. Unfortunately, regulations associated with health aspects are not internationally standardised. This can be confusing for evaluating from country to country. The worst case is when little or no attention is paid to any health and safety regulations.

3.5 Conclusions

There are alternatives available for the quasi-totality of precision cleaning applications. The choices are varied and the selection process of the most suitable compromise may be difficult because of the requirements and the evaluation parameters.

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4. Metal Cleaning

Summary

Metal cleaning is a surface preparation process that removes organic compounds, such as particulate matter, oils and greases, and inorganic soils from metal surfaces. Metal cleaning prepares parts for subsequent operations, e.g., further machining and fabrication, electroplating, painting, coating, inspection, assembly, packaging or heat treatment for surface modification. Parts may be cleaned multiple times during the manufacturing process.

The control approaches available for metal cleaning operations include solvent conservation and recovery practices and the use of alternative cleaning processes. The latter include alternative solvents and their blends, contained solvent cleaning systems, low flash point solvents, co-solvent systems, aqueous cleaners, emulsion cleaners, mechanical cleaning, thermal vacuum de-oiling, liquid carbon dioxide and “no-clean” options. Alternatives to carbon tetrachloride, CFC-113 and 1,1,1-trichloroethane must be selected and optimised for each application given the varying substrate materials, soils, cleanliness requirements, process specifications, and end uses encountered in metal cleaning.

There is still significant use of carbon tetrachloride in various cleaning processes in developing countries. These uses have been identified primarily where a low cost, non-flammable, and simple cleaning process is required, such as metal cleaning applications. While many alternatives seem obvious to improve worker exposure, total cost including environmental concerns, should be considered for any alternative.

Most CFC-113 and 1,1,1-trichloroethane used in metal cleaning applications can be replaced by existing alternatives in accordance with the Montreal Protocol. Developing countries should be able to closely follow the same scenario as the smaller companies in the developed countries. They may have an additional lag time in their own smaller industries. Each developing country will have somewhat different scenarios depending upon their unique industry basis.

4.1 Introduction

Metal cleaning applications include all applications in which metal and some synthetic parts are cleaned during manufacturing or maintenance except for those parts that are included in precision cleaning applications. Metal cleaning can be divided conveniently into 3 main sub-divisions:

- Primary production
- Periodic maintenance
- Repair and service

4.1.1. Primary Production

Some of the processes that precede metal cleaning include:

- Guillotining stock material
- Numerically controlled machining from solids
- Multistage deep drawing
- Stamping

- Forging
- Casting (of all technologies)
- Rolling
- Extruding
- Injection moulding
- Non-destructive testing
- Welding
- Vacuum forming from sheet spinning

The materials that are cleaned in primary procedures include:

- Ferrous metals and alloys
- Aluminium
- Titanium
- Other light metal alloys
- Zinc and aluminium-based die castings
- Other non-ferrous metals (e.g. copper and alloys)
- Moulded polypropylene and other thermoplastic materials
- Carbon fibre reinforced epoxy
- Glass fibre reinforced epoxy
- Other composite materials
- High alumina ceramics

Finally, examples of processes that follow primary metal cleaning include.

- Electrolytic surface treatment,
- Painting and application of other coatings
- Chemical vapour deposition
- Radio frequency coating
- Fluidised bed coating with polymers
- Application of adhesives prior to bonding
- Galvanising
- Simple surface cleaning prior to rework, repair, storage or subsequent assembly
- Application of temporary protective materials for storage and delivery protection
- Heat treatment
- Chemical surface treatment

4.1.2. Periodic Maintenance

There are many industrial processes in which plant and machinery are routinely and regularly disassembled, cleaned, reassembled, and refitted with functional materials. This can occur at the end of a working interval (end of shift, for example) or at fixed intervals. Many of these require the use of solvents, including CFC-113 and 1,1,1-trichloroethane. Examples include:

- Heating, ventilation and air conditioning systems and equipment
- Metal working machinery and equipment
- Hydraulic equipment and systems

- Adhesive spreading machinery (for impact adhesives, adhesives based on polychloroprene), epoxy resins, hot metal systems, etc.
- Silk screen stencils for general printing, solder paste printing; etc.
- Instrument pressurised oil-filling rigs using Krytox fluorolube and silicone oils
- Polymer forming equipment - injection moulding, blow moulding - vacuum moulding, etc.
- Conventional hydrocarbon oil fillings rigs - transformers, transmission systems
- Engines, etc.
- Printing machinery
- Tooling

4.1.3. Repair and Service

This is possibly the most widespread and diverse subdivision of metal cleaning and covers, for the most part, “cold solvent cleaning” in which 1,1,1-trichloroethane had become the most important cleaning agent in the early 1990s. To list examples would be to list most mechanical artifacts of the modern world. However, general areas are:

- Primary power sources
- Industrial handling equipment
- Metal working machinery - machine tools, press-tools, forging, deep drawing, etc.
- Sports and leisure

1,1,1-trichloroethane was used extensively in metal cleaning. Worldwide production in 1990 amounted to about 726,000 tonnes with 66 per cent of this total used for metal and precision cleaning. CFC-113 use in metal cleaning is less than 25 per cent of that 1,1,1-trichloroethane. In addition to conservation and recovery, this chapter describes a number of alternative materials and processes that clean metals effectively, including alternative solvents and their blends, contained solvent cleaning systems, low flash point solvents, co-solvent systems, aqueous cleaners, emulsion cleaners, mechanical cleaning (such as media blasting), thermal vacuum de-oiling, liquid carbon dioxide, steam, and “no-clean” alternatives.

4.2 Statement of Sub-sectorial Problems

In developed countries, there are no major sub-sectorial problems; essentially all uses of CFC-113 and 1,1,1-trichloroethane have suitable alternatives. Where complete phase-out has not been achieved, they are using stockpiled or recycled products. As these supplies run out, conversion to other alternatives is necessary.

In developing countries, the situation is not as clear-cut. Communication to all the users has not been as efficient as it should be, both in the urgency for action and what the alternatives are. There are also some political impediments to rapid transition to materials less harmful to the ozone layer. In some cases, where carbon tetrachloride is still being used as a cleaning solvent, governments have enacted legislation restricting the use of some materials that are suitable drop-in substitutes (see Appendix 2 and Appendix 3 for more information on government regulations of solvents).

4.3 Alternative Technology Considerations

The selection of the alternative should be based on the following five primary factors:

- Should not be an ODS.
- Should enable the enterprise to maintain a product reliability level at least equal to past methods.
- Should be economical.
- Should not create significant environmental impact.
- Should not compromise worker or consumer health and safety.

The following hierarchy of alternative classes (in order of most preferred first) has been assembled in consideration of these five primary factors to assist enterprises with their decision:

1. "No-clean", keep-clean
2. Aqueous/hydrocarbon-surfactant cleaning
3. Organic solvent cleaning (with solvents less toxic than non-ozone-depleting halogenated solvents)
4. Non-ozone-depleting halogenated solvents (trichloroethylene, perchloroethylene, methylene chloride, HFC, HFE, the two latter often mixed with 1,2-trans dichloroethylene)
5. Organic solvent cleaning (with solvents more toxic than non-ozone-depleting halogenated solvents)
6. HCFC-225
7. n-Propyl bromide¹
8. HCFC-141b²
9. PFCs

4.4 Environmental, Health, and Safety Constraints

Each alternative has some advantages and disadvantages under environmental, health, and safety constraints. However, all those listed are more favourable than continued use of ODS.

“No-clean” technologies may offer the least environmental effects on first appearances. However, it is important to consider any upstream and downstream effects that may cause additional processes having detrimental effects.

Aqueous technologies must take into account proper treatment of waste water, waste materials that are generated from the process, and additional energy costs.

Hydrocarbon materials must include precautions for proper fire and explosion control; in addition, these are VOCs and may be regulated in many countries or face future regulation. Proper waste management is also needed.

Chlorocarbons, while often-potential drop-in replacements, should include proper controls for worker exposure, and minimising emission to the environment. Waste management is also mandated in most countries.

¹ Still under review by the Scientific Assessment Panel (See Appendix 1)

² Regulated in some developed countries

HFC and HFE solvents, largely because of their cost, should also have tight emissions control. In many cases, these products also contain a chlorocarbon (1,2-trans-dichloroethylene), which makes them more effective cleaners. They should be handled much the same as chlorocarbons.

HCFC-225 is a low ODS, which will be phased out later. However, it will provide a reasonable term interim solution.

n-Propyl bromide has recently been introduced as an ozone-depleting alternative and is still undergoing review by the Scientific Assessment Panel. It is also toxic (see Appendix 1).

HCFC-141b is a short term-solution; it has already begun to be phased out in some developed countries.

4.5 Conclusion

In general, the phase-out of CFC-113 and 1,1,1-trichloroethane has been achieved in developed countries, with most users finding alternatives in the above sectors. In developing countries, the challenge is to educate the user base, and in some instances, the regulatory agencies involved.

4.6 Sources of Additional Relevant Information

Internet web pages

International Workshop on Solvent Substitution

http://www.exchangemonitor.com/dec_scott.pdf

Solvent Substitution Data Systems (US EPA)

<http://es.epa.gov/ssds/ssds.html>

Solvents Discussion Group (Yahoo)

http://groups.yahoo.com/group/solvents_group/

The European Solvents Industry Group

<http://www.esig.org/>

The European Chlorinated Solvent Association

<http://www.eurochlor.org/chlorsolvents/generalinfo/info.htm>

Halogenated Solvents Industry Alliance (USA)

<http://www.hsia.org/>

CleanTech Magazine and Annual Exposition

<http://CleanTechCentral.com/>

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5. Dry Cleaning

Summary

Ozone depleting solvents, CFC-113, and 1,1,1-trichloroethane were used in specialised segments of the dry cleaning industry. CFC-113 was used primarily for delicate fabrics and those with sensitive dyes and trimmings. 1,1,1-Trichloroethane was used mostly in the leather and suede applications in North America and, to a limited extent, for general dry cleaning elsewhere.

It is believed that the developed countries have completely substituted these solvents either with existing solvents, such as perchloroethylene, or to some of the new solvents mentioned in this report and prior editions. For developing countries there was no evidence that 1,1,1-trichloroethane was used as a dry cleaning solvent, except possibly in E. Asia, and very little, if any, CFC-113.

5.1 Introduction

CFC-113 was used as a dry cleaning solvent because of its low toxicity, stability, non-flammability, and relatively low boiling point, which minimised energy requirements during drying and distillation. In addition, its low solvency power (31 Kauri Butanol Value) enabled the cleaning of fabrics with sensitive dyes and trimmings that would be damaged if cleaned with stronger solvents. CFC-113, used in conjunction with leather oils, was ideal for cleaning fur, suede, and leather garments. It is estimated that less than 3 per cent of dry cleaning is currently undertaken in CFC-113, half of which is drawn from private stockpiles with the rest newly purchased.

1,1,1-Trichloroethane only found minimal use as a dry cleaning solvent because of its high solvency power (Kauri Butanol 124). Although it removed soiling easily, it damaged some plastic trimmings, pigment prints, and bonded fabrics. The higher capital cost of the machines, strong solvent odour and its low stability further limited its popularity. Very few machines remain in use.

5.2 Statement of Sub-sectorial Problems

Since most dry cleaning was done using perchloroethylene, and the ODSs, CFC-113, and 1,1,1-trichloroethane, were used mostly in specialised applications, there have not been any major problems associated with the availability of a suitable dry cleaning solvent. There has been some concern over the perceived toxicity of perchloroethylene, and efforts to substitute alternative solvents have met with some resistance. However, a few processes are becoming accepted into the market place and may offer an alternative to having only one dry cleaning solvent.

5.3 Alternative Technology Considerations

The selection of the alternative should be based on the following five primary factors:

- Should not be an ODS.
- Should enable the enterprise to maintain a product reliability level at least equal to the past methods.
- Should be economical.
- Should not create significant environmental impact.

- Should not compromise worker or consumer health and safety.

The following hierarchy of alternative classes (in order of most preferred first) has been assembled in consideration of these five primary factors to assist enterprises with their decision:

5.3.1. Perchloroethylene

Perchloroethylene, the most widely used dry cleaning solvent, has been used in this application for over 60 years, during which time the systems for its safe use have become highly developed. For dry cleaners that are seeking to replace their CFC-113 or 1,1,1-trichloroethane machines, perchloroethylene is a logical and practical choice. Its higher solvency power than CFC-113 means that it is not suitable to clean a minority of the fabrics, trims, etc., that can be cleaned in CFC-113. It is an adequate replacement for 1,1,1-trichloroethane.

Some studies have implicated perchloroethylene as a possible carcinogen although recent toxicological and epidemiological evidence indicates that this is either not proven or due to species differences not relevant to humans. In addition, it is important to bear in mind that modern perchloroethylene machines are extremely efficient and usually result in low solvent emissions. Nonetheless, the use of perchloroethylene in dry cleaning may be regulated in some countries, regions, or localities. For example, the U.S. EPA set national emissions standards for perchloroethylene in September 1993 that apply to both new and existing perchloroethylene dry cleaning facilities.

5.3.2. Petroleum Solvents (White Spirit, Stoddard Solvent, Etc.)

The flammability of petroleum solvents effectively precludes their use in shops, although with proper precautions, they can be a substitute for CFC-113 on many fabrics. In Australia, for example, a fabric labelling convention has been introduced that designates white spirit as a substitute for CFC-113 in the dry cleaning of specific fabrics (Standards Association of Australia 1987).

Petroleum solvents include white spirit, Stoddard solvent, hydrocarbon solvents, isoparaffins, n-paraffin, etc. Depending on the solvent, characteristics such as flash point, solvency (Kauri Butanol Value), distillation temperature etc. will vary. White spirit and Stoddard solvent were developed for dry cleaning applications 40 – 50 years ago and have been used, to some extent, in the U.S., Europe, Japan and Australia. However, their use has been gradually decreasing over time because of substitutions made to non-flammable solvents and because of regulations restricting emissions of volatile organic compounds. In addition, despite epidemiological studies, there are unresolved issues concerning the toxicity of some petroleum solvents.

Recent improvements in dry cleaning equipment to maximise recovery of cleaning solvents, while minimising emissions, have resulted in increases in the use of flammable solvents. In addition, new petroleum solvents that have lower odour and toxicity are being marketed.

5.3.3. Other Hydrocarbon Solvents

Recently, a large chemical manufacturer introduced a synthetic, high purity hydrocarbon solvent. Some of the properties, which may make it a good dry cleaning solvent, include good cleaning power, low odour, long service life, high flash point, and low toxicity.

A relatively high flash point of 64 °C (147 °F) provides a greater margin of safety over most other hydrocarbon solvents, thereby reducing building fire suppression requirements in some areas. This solvent is currently in use at dry cleaning facilities and the following properties have been observed:

- Compatible with closed-loop, dry-to-dry machines traditionally used with perchloroethylene (PERC) and petroleum solvents
- Compatible with common additives
- Requires no deodorants since it is virtually odourless
- Cycle time comparable to that of Stoddard solvent and slightly longer than PERC
- Little or no plant/building modifications except for the approval from the Fire Prevention Authority
- Releases dirt to carbon/clay filters improving cleanliness and prolonging solvent life

Potential users of this or any other flammable solvent should determine their acceptability given local fire regulations.

5.3.4. Hydrochlorofluorocarbons (HCFCs)

A number of HCFCs and HCFC blends are currently available commercially for use in solvent applications. These include HCFC-123, HCFC-141b, and HCFC-225. These HCFCs have good stability, excellent solvency, and non-flammability and some HCFCs are suitable for cleaning those delicate fabrics that currently depend on CFC-113. Due to its status as a suspected carcinogen, HCFC-123 is not being marketed for use in solvent applications and is therefore not a possible alternative to CFC-113 and 1,1,1-trichloroethane. In addition, HCFC-141b is not a recommended alternative, especially for 1,1,1-trichloroethane, because it has an ozone-depletion potential comparable to that of 1,1,1-trichloroethane. HCFC-225, which is a blend of the ca and cb isomers, has a similar boiling point to CFC-113 and is proving suitable for cleaning many sensitive fabrics. Because of dry cleaners' concerns for the solvent cost/selling price ratio, the cost of the blend (currently very high) will determine how readily it is used. HCFC-122a is used in some countries with equipment similar to CFC-113. In these countries it is considered to have an acceptable low level of toxicity. Therefore, it may be used as a replacement for CFC-113, subject to relevant regulations. It should be noted however, that HCFCs are transitional alternatives subject to phase-out under the Montreal Protocol.

5.3.5. Methyl Siloxane

Silicone solvents have recently been developed for use in dry cleaning operations. One of the products currently being marketed is decamethylcyclopentasiloxane. There are several business models being developed to market these products in the dry cleaning sector. While these materials do work well, they must be used in equipment equivalent to the hydrocarbon needs, as they have flash points of 76 °C. Due to the flammability of the solvent, equipment design follows a typical Class IIIA hydrocarbon machine design, meeting electrical standards for explosion proof /non-sparking operation with operation under vacuum during high temperature portions of the cycle (drying and distillation). Some modifications have been made compared to standard HC machines in order to accommodate different physical properties. There are several efforts being made to modify other technologies such as vacuum systems

that would also overcome some of the flammability concerns. In the U.S., unlike the European Union, the solvents are not regulated as VOCs.

5.3.6. Glycol Ethers

Glycol ethers have been introduced as dry cleaning solvents in the late 1990s. They can work in hydrocarbon machines under similar conditions. Since they are miscible with water and hygroscopic, they tend to absorb moisture from the garments and this can cause shrinkage.

5.3.7. nPB

n-Propyl bromide was introduced in 2001 in an experimental dry cleaning machine. This solvent is prohibited for such use in some European countries. It is not recommended because of the uncertainty around its toxicity and ozone-depletion potential (see Appendix 1).

5.3.8. Liquified Carbon Dioxide

Several companies have introduced experimental carbon dioxide dry cleaning technologies. They have been somewhat successful in implementing a small number of machines but still struggle with the higher capital cost of this technology. Special detergents must be added to the liquid carbon dioxide. A typical carbon dioxide machine will cost 3 to 4 times that of a perchloroethylene machine. However, the cost of running the machine is similar to the latest 4th and 5th generation perchloroethylene machines. In this sector there are also several business models that are being tested to implement the technology. These typically include a licensing and leasing agreement to use the machine and the technology. A fully commercial machine is not expected before 2005.

5.3.9. Wet Cleaning

One promising alternative to any type of solvent is wet cleaning. It uses a minimum of water together with some detergents. It can handle 60 to 70 per cent of the stains, but it must still be associated with solvent dry cleaning for some more severe duties. Its cost is currently higher than dry cleaning.

5.3.10. Centralised Processing Facilities

The establishment of centralised cleaning facilities could augment the controls on solvent losses that can be achieved at small, individual dry cleaning establishments. At centralised facilities, additional investments in control devices and standardised operation and maintenance practices can lead to more efficient solvent use.

5.4 Environmental, Health, and Safety Constraints

For many years, dry cleaning machines have been totally enclosed; incorporating filtration, distillation, and refrigerated recovery systems allowing solvents to be continuously recycled.

The development of the improved equipment has allowed dry cleaners to substantially reduce the emissions or losses of dry cleaning fluid from their operations. This technological development has also enabled the use of previously unsuitable materials to be used. The use of most new alternatives will require the purchase of new equipment.

Retrofitting a CFC-113 or a 1,1,1-trichloroethane dry cleaning machine to one of the new alternative solvents is not a recommended practice. With the advances made

since the phase-out started, a new machine will pay for itself in improved operating efficiency.

5.5 Other Relevant Information

Carbon tetrachloride is being used in some Article 5(1) countries for fabric cleaning applications. Use of carbon tetrachloride in developed countries was ended some 35 to 40 years ago on health and safety grounds. Carbon tetrachloride is highly toxic and a suspected human carcinogen having an ozone-depleting potential of 1.3 and its use in this application should be discontinued.

Any machines using carbon tetrachloride that do not adequately dry clothes, prior to pressing, require immediate maintenance or replacement. The use of another solvent in a machine designed for use with carbon tetrachloride is not advisable and replacement is recommended. In exceptional circumstances, it may be possible to modify a machine for use with perchloroethylene. This is a matter for individual assessment and consultation with the machine manufacturer.

5.6 Conclusion

Major reductions in CFC-113 and 1,1,1-trichloroethane usages for dry cleaning have resulted from the replacement of cleaning machines designed for these solvents. Perchloroethylene and hydrocarbon solvents are the logical replacement, dependent on the solvency power required.

No use of CFC-113 or 1,1,1-trichloroethane is necessary in the dry cleaning industry. Few, if any, CFC-113 machines were installed in Article 5(1) countries.

Carbon tetrachloride should be discontinued.

For general dry cleaning, perchloroethylene is the recommended alternative. While the cost of state-of-the-art, totally enclosed, perchloroethylene machines is likely to be high, some countries are manufacturing dry cleaning machines, some of which may have high emissions. Specialist cleaning of delicate, intricate, or animal-skin items can be achieved using hydrocarbon or HCFC solvents. Equipment for use with hydrocarbon solvents is available in totally enclosed or open transfer variants. Given the lower cost of the latter, these systems are likely to be favoured for specialist cleaning in developing countries.

5.7 Sources of Additional Relevant Information

Brazil ANEL

<http://www.anel.com.br/>

International dry cleaners' conference

<http://www.idcnews.org/>

International Fabricare Institute

<http://www.ifi.org/>

EPA Technology Innovation Office

<http://207.86.51.66/>

CINET (International Committee for Textile Care)

<http://www.cinet-online.net/>

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6. Adhesives

Summary

While there is no drop-in replacement for 1,1,1-trichloroethane in adhesive bonding products, a variety of solvent-based and non-solvent adhesives provide high performance for specific applications. In many cases, changes to previous operating procedures must be made, but in general these changes are not very restrictive. Careful selection of available alternatives is important to adequately meet performance, cost, regulatory, and worker health criteria.

6.1 Introduction

Prior to the phase-out in developed countries, 1,1,1-trichloroethane was the major ODS used in adhesive formulations because it is non-flammable, dries rapidly, does not significantly contribute to air pollution, and performs well in many applications, particularly foam bonding. While there are no drop-in replacements, there are alternative solvents that can be selected for specific applications. Where flammability is an issue, other halogenated solvents can be used as direct substitutes. If other environmental or safety concerns are present, then alternative technology is often available.

1,1,1-trichloroethane has almost been eliminated in developed countries and will be terminated after the available stocks are consumed. However, in developing countries, it is still being used at a declining rate. The reason for such reduction in use is twofold: 1) limited availability of the solvent through imports and 2) awareness of the Montreal Protocol.

A partial list of applications where 1,1,1-trichloroethane-based adhesives are used includes packaging, non-rigid and rigid bonding, construction, tapes, transportation, and consumer adhesives. The largest use of halogenated solvents is in contact cements and rubber products.

For a detailed technical assessment of using 1,1,1-trichloroethane in adhesives, see previous STOC Assessment Reports published in 1992, 1994, and 1998.

6.2 Statement of Sub-sectorial Problems

1,1,1-Trichloroethane has several physical characteristics that provide desirable performance properties for adhesive applications. It has been used as the preferred solvent primer for many years in contact bonding adhesives. In fact, this solvent has better properties in all respects than all other, non-ozone depleting candidates, except that it has an ozone-depletion potential. Almost all the conventional solvents fall in the category of Volatile Organic Compounds (VOCs). VOCs are regulated in different ways by governmental regulations. In some areas the VOCs are controlled by threshold concentrations, while in others are limited by substitution of less reactive solvents. The environmental regulation authorities of the countries using these solvents generally enforce this. There are no unique thresholds or limits for these solvents.

The physical properties of many solvents used are provided in Appendix 3 and in the 1998 STOC Assessment Report.

In general, 1,1,1-trichloroethane is used as an active solvent in contact adhesives and spray adhesives, where a good green bond or initial bond, is desired, as in the manufacture of foam cushioned, or plastic laminated furniture.

The options available for solvent reduction in adhesives fall into two broad categories: established technologies and new technologies. Established technologies include other solvent-based adhesives, water-based adhesives, hot melt systems and solvent recovery or destruction systems in continuous operations. New technologies include radiation cured adhesives, high solids adhesives, powders and reactive liquids. These technologies are discussed in further detail in the previous assessments.

6.3 Alternative Technology Considerations

The selection of the alternative should be based on the following five primary factors:

- Should not be an ODS.
- Should enable the enterprise to maintain a product reliability level at least equal to the past methods.
- Should be economical.
- Should not create significant environmental impact.
- Should not compromise worker or consumer health and safety.

The preferred alternatives for consideration are as follows:

1. "No-solvent", hot melt radiation curable
2. Aqueous, emulsions
3. Organic solvents (low ozone-depleting, low toxicity, low flammability solvents)
4. Non-ozone-depleting conventional halogenated solvents (TCE, MC, PCE,)

An extensive discussion of specific alternatives for replacement of 1,1,1-trichloroethane is provided in the 1998 STOC Assessment, including the following:

- *Other solvent-based adhesives*
 - The use of other solvents, such as acetone, ethyl acetate, heptane and toluene; these are characterised, generally, as high-VOC, highly flammable and may be costly. Use is limited for economic reasons.
- *Water-based adhesives*
 - Water-based adhesives are primarily characterised as solutions, latexes or emulsions, with latexes providing the best performance and versatility, due to the incorporation of synthetic binders in the formulations.
 - Water-based adhesives provide good durability, water-resistance and adhesion for non-porous to porous surface bonding applications. Some problems persist for non-porous to non-porous surface bonding, due to difficulty in evaporating water from such surfaces.
 - Water-based adhesives bond moist surfaces well.
 - Problems with handling during shipment, storage and manufacturing, corrosion of transfer pipes, and material homogeneity require special precautions.

- *Hot melt adhesives*
 - Major applications are bookbinding, packaging, textiles, and product assembly, including construction glazing and automotive door panel and carpet installation.
 - Advantages include good gap filling effectiveness, low hazard in material handling and low overheads.
 - Hot melts have poor specific adhesion to a number of substrates, creep under load over time and have poor high temperature strength.
- *Radiation cured adhesives*
 - Application areas include electronics (printed circuit boards), communications, consumer products, transportation, packaging, medical and dental uses and pressure sensitive tapes.
 - Applications are limited to close to the line-of-sight of the radiant energy.
- *High solids adhesives*
 - Polyethylene and polyester systems have been successfully used in laminate applications.
 - High solids adhesives can be applied using existing equipment at normal line speeds, with minor modifications.
 - Advanced products have been successfully used in structural applications, such as on aircraft wings, but require refrigeration for storage, shelf life control and training or practice in application.
 - These materials have not been used successfully in bonding rubber assemblies.
- *Powders*
 - One-part epoxy, urethane and natural powders can be applied to a pre-heated surface that cures the materials, but they must be refrigerated to maximise shelf life.
- *Non-volatile solids and liquids and reactive liquids*
 - Moisture cured adhesives require no solvent carrier, and cure upon exposure to the humidity in ambient air.
 - In general, these adhesives provide high performance for joining metallic and other non-porous materials.
 - Reactive liquid adhesives provide high performance for structural bonding applications, without the use of a solvent carrier.

Generally, fluorocarbon solvents do not have adequate solvency for use in adhesive formulations.

6.4 Cost of Alternatives

Substitution costs are driven by the following factors:

- Raw material
- Capital equipment

- One element of cost may be ventilation or vapour recovery equipment, if a VOC-containing system is selected
- R&D validation
- Waste disposal

Balanced against the potentially significant cost of conversion is the total life cycle cost savings gained through lower space and energy requirements, increased productivity and higher throughput. Because radiation cured adhesives have a long shelf life, their use leads to production of a more reliable product, lower rejection rates and labour costs, and reduced clean-up and inspection times. In general, high solids adhesives cost more per gross weight, but outperform their solvent-borne counterparts.

6.5 Environmental, Health, and Safety Constraints

There are a number of environmental and energy implications to replacing 1,1,1-trichloroethane-based adhesives with alternatives. Returning to the use of other solvent-based adhesives will affect local air pollution and worker safety unless precautions are taken. In the applications, where non-flammability is important in high-risk areas, 1,1,1-trichloroethane has been replaced by non-ozone depleting perchloroethylene and methylene chloride. Methylene chloride seems to be the better choice for its higher solvency and fast evaporation rate.

Water-based adhesives have a number of characteristics that make them attractive substitutes. As they contain no volatile organic solvents, water-based adhesives do not contribute to local smog problems and are non-flammable. They can, however, emit small quantities of hydrocarbons, ammonia, and emulsion-stabilising substances. In ideal situations, these pollutants can be removed, to some extent, using, for example, wet scrubbers.

From the energy perspective, drying ovens used for solvent-based systems generally are adequate to handle water-based adhesives. Increased air flow rates, temperatures and longer oven-bake cycle times may be required to evaporate water, however, so process flow can be affected and energy usage may increase.

Hot melt adhesives also have several environmental and energy advantages. As no solvents are used in hot melts, they do not contribute to smog formation. In part, because no drying oven is needed, hot melt pressure sensitive adhesives require far less energy to process than most other adhesive types. The percentage of solids in the formulation directly influences the amount of energy saved; this percentage varies depending on the application.

The advantages of radiation-cured adhesives may include low energy costs and reduced emission of waste effluents, polluting gases, and liquids.

Both moisture-cured adhesives and reactive liquids achieve compliance with VOC regulations because they contain no solvents. Moisture-cured systems also need no dryers, and thus save energy. The application equipment is more compact than that of solvent-based systems, but moisture-cured adhesives cannot use existing solvent application equipment. Moisture-cured adhesives and sealants, especially silicones, evolve small amounts of methanol, acetic acid or other products from the

polymerisation. There is some concern that the catalysts used with reactive liquid systems are, in some cases, hazardous or toxic substances.

n-Propyl bromide is being used to replace methylene chloride and 1,1,1-trichloroethane in some adhesive formulations. This is not recommended because of the unknown toxicity and ozone-depleting potential (see Appendix 1).

6.6 Conclusion

There are no technical barriers to replacing 1,1,1-trichloroethane in adhesive formulations. Suitable substitutes are available for reformulating current adhesives. However, choices may need to be made to address relevant factors such as flammability, volatile organic compound restrictions, and worker exposure.

6.7 Sources of Additional Relevant Information

<http://www.ascouncil.org/>

<http://www.adhesionsociety.org>

Federation of European Glues and Adhesives Industries

<http://www.feica.org>

E-mail addresses of STOC members who can offer advice

jamertens@dow.com

7. Aerosols applications

Summary

HCFC-141b had emerged as a lead replacement candidate for CFC-113, CFC-11, and 1,1,1-trichloroethane since their non-Article 5(1) country phase-out in 1996 in aerosol formulations as an active ingredient or as a solvent. However, HCFC-141b has an ozone-depletion potential about equal to that of 1,1,1-trichloroethane; its use has therefore been phased out in Europe since the beginning of 2002 and is scheduled in the United States at the end of 2002. The replacement solvents include petroleum distillates, water-based products, organic solvents, HFCs and HFES. However, the use of HCFC-141b may continue in Article 5(1) countries until its scheduled phase-out date of 2040.

7.1 Introduction

In this chapter, the solvent alternatives for CFCs are discussed. The CFC-11/12 propellants alternatives such as HFC-134a, HFC-152a, dimethylether, hydrocarbons, and inert gas are covered in the Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride Technical Options Committee reports.

In an aerosol package, the contents are stored under pressure in a metal container and dispensed in a controlled manner by activating a valve. In general, the components of an aerosol are the active ingredient, the solvent or carrier, and the propellant. The active ingredient is responsible for the effectiveness of the product (i.e., the ingredient that allows a cleaner to clean); the solvent or carrier dissolves all ingredients in the formulation to allow for a uniform dispensing of the product; the propellant expels the contents from the can. In some cases, the solvent is also the desired product to be dispensed, such as for aerosol cans designed for cleaning applications.

The growth in the use of aerosol packaging has considerably slowed down since the 1980s. The most recent report indicates that aerosol-packaging units reached the 3.2 billion mark in the U.S. in 1997 after a 2.3 per cent decline in 1995. The most popular uses (USA) of aerosol packages are:

- Personal Products (32%)
- Household (27%)
- Automobiles/Industrial (13%)
- Paint (14%)
- Food (7%)
- Insecticide spray (6%)

The use of solvents in aerosols may be of importance only in such applications as automobiles and industrial, paint, insecticide spray and some household uses. The most popular solvent in these applications was 1,1,1-trichloroethane. CFC-113 was used in electrical contact cleaning where non-flammability was essential and for printed circuit board defluxing with additives. HCFC-141b and its azeotropic blends with alcohol are currently used as a substitute for CFC-113 and for 1,1,1-trichloroethane. Because HCFC-141b has an ozone depletion potential about equal to that of 1,1,1-trichloroethane, its phase-out schedule is moved up in non-Article 5(1) countries. HCFC-141b was phased-out in Europe from January 1, 2002 and will be in

the United States from December 31, 2002. The replacement solvents include petroleum distillates, water-based products, organic solvents, HFCs, and HFEs.

7.2 Statement of Sub-sectorial Problems

In developed countries, there are no major sub-sectorial problems; essentially all uses of CFC-113, 1,1,1-trichloroethylene, and CFC-11 have been eliminated in aerosol formulations by either low ozone-depleting potential solvents or zero ozone-depleting potential alternatives. Major efforts are now under way in developed countries to replace ozone-depleting HCFC-141b from these applications by suitable substitutes such as HFCs, HFEs, hydrocarbons, chlorocarbons, alcohol, and water-based products.

In developing countries, HCFC-141b use may continue until its phase-out date. Some of the environmentally safe, non-flammable and low toxicity substitutes such as HFCs and HFEs may be too expensive for use in most applications and may result in the use of flammable or more toxic chlorocarbon substitutes.

7.3 Alternative Technology Considerations

The selection of the alternative should be based on the following five primary factors:

- Should not be an ODS.
- Should enable the enterprise to maintain a product reliability level at least equal to the past methods.
- Should be economical.
- Should not create significant environmental impact.
- Should not compromise worker or consumer health and safety.

Most aerosol products requiring a solvent, used in developed countries, are currently employing one of the substitutes listed in Table 1. Most of the low-cost (petroleum distillates, hydrocarbons, alcohols, ketones, and dimethyl ether) are, unfortunately, more flammable than the products they are replacing. The flammability is also a function of the propellant, butane, propane and HFC-152a being more flammable than carbon dioxide, nitrous oxide or the traditional CFC-11/CFC-12 mixture.

Table 1. Substitute Solvents for CFC-113, CFC-11 and 1,1,1-trichloroethane in Aerosols

Solvent Substitutes	Major Product Applications			Flammability
	Auto & Industrial	Pest	Household	
Petroleum Distillates	yes	yes	yes	high
Water Based	yes	yes	yes	none
Organic Solvents (alcohols, ketones, aromatic hydrocarbons)	yes	yes	yes	high
Chlorinated Solvents	yes	yes	yes	none
HCFCs	yes	yes	yes	none
HFCs	yes	yes	yes	none
HFEs	yes	yes	yes	none

7.3.1. Petroleum Distillates

Due to the high flammability of the petroleum products, reformulation can be performed only in selected applications and with proper explosion-proof equipment. Commercially available products reformulated with petroleum distillates and other hydrocarbon solvents exist for various automotive products such as tyre cleaners, lubricants, spray under-coatings and in household products, such as water repellents, shoe water-proofers, glass frostings, and insecticides. Extreme care must be exercised in both the manufacture and use of these products to reduce the risk of explosion. These solvents are classified VOCs and their use may be restricted in some geographic areas.

7.3.2. Water-based Systems

Reformulation from 1,1,1-trichloroethane or CFC-113 to water-based systems can be performed in a number of applications, including shoe polishes, foggers (partial or total release insecticides used to control infested rooms), mould release agents, and fabric protectors. The major disadvantage and concerns of reformulation of 1,1,1-trichloroethane or CFC-113 to water-based systems are the effectiveness of the final products. These concerns arise from several fundamental differences in the systems. For example, it is generally agreed that water-based foggers are less effective because they do not disperse well and they result in large particle sizes. These factors make the foggers less effective than those that utilise 1,1,1-trichloroethane since the water tends to be ineffective at penetrating the exoskeleton of insects. Tests are currently underway to produce water-based solvent mixtures, which will be able to overcome this problem. Use of dimethyl ether as a propellant and solvent might greatly improve the feasibility of a water-based formulation. Other drawbacks associated with water-based aerosol products include long drying times and inability to sufficiently wet the surface being sprayed due to the high surface tension of water. The relatively slow evaporation rate of water, as compared with that of CFC-113 or 1,1,1-trichloroethane, results in an increased drying time.

Despite these drawbacks, water-based aerosol formulations are becoming more common in a wide variety of applications, especially among those unable to use or wanting to avoid the use of flammable solvents, HCFCs, and chlorinated solvents.

7.3.3. Organic Solvents

Many alternative organic solvents can be used to replace CFC-113 or 1,1,1-trichloroethane in aerosol-cleaning applications. These alternative solvents include aliphatic and aromatic hydrocarbons, alcohols, ketones, and terpenes. These solvents are capable of removing a wide variety of contaminants and all are currently used in commercially available aerosol products. This strong cleaning power, coupled with the ability to solubilise other active ingredients, makes these alternative solvents attractive substitutes for CFC-113 and 1,1,1-trichloroethane.

There are two primary drawbacks associated with the reformulation of aerosol products using organic solvents—flammability and environmental impact. All of the aforementioned organic solvents are flammable and must therefore be used with extreme caution to reduce the risk of explosion and fire. While many users are able to safely implement flammable formulations with only minor process and handling changes, others may not be able to overcome the risks associated with the

flammability of the solvents. For example, flammable solvents are not a viable alternative for the *in-situ* cleaning of live electrical equipment. The major environmental concern associated with these organic solvents is their impact on the formation of smog and other ground-level pollution. These solvents are classified as VOCs and their use is severely restricted in some geographic areas. Nonetheless, where flammable solvents are acceptable, reformulation using organic solvents is an attractive option.

7.3.4. Non-ozone-depleting Chlorinated Solvents

Reformulating aerosol products to use non-ozone depleting chlorinated solvents in place of CFC-113 or 1,1,1-trichloroethane is an option in limited applications. The chlorinated solvents that might be used are trichloroethylene, perchloroethylene, and methylene chloride. The primary benefits associated with these alternatives are their non-flammability and high solvency.

Potential formulators and users of aerosols containing these solvents must be aware of their associated human health risks. All three of these alternatives are toxic and have accordingly low occupational exposure limits.

7.3.5. Without a Solvent

In some cases where CFC-113 or 1,1,1-trichloroethane is used only as a solvent or carrier, and not as an active ingredient, it may be possible to reformulate the aerosol product to function without the use of a solvent. In these non-solvent systems, solely the force of the propellant disperses the active ingredient of the product. Several manufacturers of aerosol mould release agents, with improved performance in some applications, are currently marketing such a formulation. In this case, there is no longer any possibility of the solvent attacking plastics or metals with which it comes into contact. However, it is also possible to obtain inferior performance, primarily because of the uneven dispersion of the active ingredient, which phenomenon may occur in the absence of a solvent carrier.

7.3.6. HCFCs

HCFC-141b with acceptable toxicity and excellent solvency has successfully replaced CFC-113 and 1,1,1 trichloroethane in aerosol applications in developed countries and in some Article 5(1) countries. However, because HCFC-141b has an ozone depletion potential about equal to that of 1,1,1-trichloroethane and other alternatives have come to market, it is being phased-out in developed countries sooner than the original 99.5 per cent phase-out schedule of 2020. HCFC-141b has been phased-out in Europe from January 1, 2002 and will be in the United States from December 31, 2002. The replacement solvents include petroleum distillates, water-based products, organic solvents, HFCs, and HFEs.

7.3.7. HFCs/HFEs

Manufacturers of fluorocarbons have introduced a family of new hydrofluorocarbon (HFC) and hydrofluoroether (HFE) solvents with no ozone-depletion potential. These products are now commercially available. They are- hydro decafluoropentane (HFC-43-10 mee), 1-methoxy-nonafluorobutane (HFE-449s1) and 1-ethoxy-nonafluorobutane (HFE-569s12).

HFCs and HFEs are non-flammable and have low toxicity, good stability, and compatibility with many metals and synthetic materials. The only drawbacks of both HFCs and HFEs are lower solvency than CFC-113 or 1,1,1-trichloroethane and higher cost. However, azeotropes of these compounds with hydrocarbons, alcohols, chlorocarbons, and ketones provide significant cleaning performance enhancement and at the same time maintain compositional stability and non-flammability in use.

Several aerosol formulators have introduced aerosol packages using both of the new product categories, HFCs and HFEs, and their azeotropes.

7.4 Environmental, Health, and Safety Constraint

HCFC-141b has an ozone depletion potential and is scheduled for phase-out.

Petroleum distillates and organic solvents have low toxicity but are highly flammable and may require proper explosion proof equipment. In the United States, all of these solvents are classified as VOCs and their use may be restricted in some geographical areas.

Non-ozone depleting chlorocarbon solvents (trichloroethylene, perchloroethylene and methylene chloride) have high toxicities and are considered by some as suspected carcinogens.

7.5 Conclusion

There are no barriers in replacing CFC-113 and 1,1,1-trichloroethane in aerosol formulations. However, replacement of HCFC-141b with totally non-flammable low cost alternatives will be a challenge.

7.6 Sources of Additional Relevant Information

E-mail addresses of STOC member who can offer advice:

abid.n.merchant@usa.dupont.com

f2samej@attglobal.net

8. Miscellaneous Applications

Summary

There are a number of miscellaneous industrial and laboratory applications that have not been addressed in previous sections of this report. Relatively small quantities of CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride are employed in most of these applications.

In many cases, the alternatives are readily available but their selection and validation may require extensive effort. In other areas, some ODSs are still necessary even though significant progress has been made towards a complete phase-out.

8.1 Introduction

A number of miscellaneous applications that have not been addressed in the other sub-sectors are discussed here. Specific applications include: oxygen systems cleaning, space vehicle manufacturing, bearer media, component drying, riveting and machining, aeroplane hydraulic systems, leak detection, fabric protection and coating, laboratory testing, mould release agents, motion picture film cleaning, and critical military applications.

Primary ODSs used in these applications include: CFC-113, 1,1,1-trichloroethane and carbon tetrachloride. ODSs HCFC-141b and HCFC-225 have been used as alternatives for several applications, with HCFC-141b now being phased out in the U.S. and the European Union. HCFC-225 is still being introduced to replace other ODSs in some critical applications.

In some applications of laboratory analyses, the parties have granted an exemption for continued use of specified ODSs. The exemptions are subject to review and alternatives are being investigated.

8.2 Statement of Sub-Sectorial Problems

8.2.1. Oxygen Systems Cleaning

The use of oxygen, in gaseous and liquid form, involves a degree of risk because oxygen vigorously initiates and supports combustion when in contact with many substances. Thus, a high level of cleanliness is a prerequisite for oxygen system components. High-pressure liquid oxygen is particularly susceptible to contamination and very few solvents tested for use in these systems pass the required liquid oxygen impact test.

CFC-113 was the solvent of choice for many years in cleaning oxygen systems. Some companies have used HCFC-141b as a transitional solvent, even though it, too, is being phased out. Alternative cleaning methods include aqueous systems with or without ethanol. Some organisations have started using solvents containing HFEs, HFCs, and HCFC-225, although the HFEs and HFCs generally have low solubilisation of contaminants. Often, processes that use a more aggressive cleaning agent first, followed by an ultra-pure rinse with water or a fluorinated compound, have been developed. Ultrasonics have been introduced in tank processes to improve cleaning effectiveness.

CFC-113 and 1,1,1-trichloroethane have also been used to inspect for cleanliness of oxygen systems. The solvent is flushed through or over the cleaned part and then analysed for extracted non-volatile material. It is critical that the extraction solvent has sufficient solvency power to remove all suspected contaminants and that the solvent itself does not remain on the cleaned parts to cause system failures. In some cases, ODSs are still being used. Alternatives include HCFC-225, trichloroethylene and multi-step processes including initial flush with alcohol, followed by ultra-pure water, HFE, or HFC.

8.2.2. Space Vehicle Manufacturing

Manufacturing of solid rocket motors still requires some 1,1,1-trichloroethane for insulator adhesive activation and cleaning and preparing for bonding of rubber and phenolic insulators. Non-ozone depleting cleaners for propellant mix and cast tooling have been successfully implemented following static test verification in a full-scale motor, confirming adequate performance of a commercial range of degreasing fluids.

8.2.3. Bearer Media

Dipping a part in an ODS containing a small amount of lubricant or other desired coating has been used to obtain a very thin coating. Spraying, rolling or other mechanical application of the neat active ingredient has sometimes been successful, as has the use of water-based emulsions or alternative carrier solvents. Selection of an alternative lubricant or coating may be necessary to optimise alternative application techniques.

8.2.4. Vapour-phase Soldering

Vapour-phase soldering alternatives include avoiding the use of a secondary vapour blanket by using batch equipment designed to work without a vapour blanket or using a secondary vapour blanket that is not ozone depleting. Fluorocarbon liquids have been developed and could meet this requirement. This technique is more expensive and has a relatively high global warming potential. Other options, where specifications and throughput allow, are infrared and convection soldering.

8.2.5. Component Drying

Many precision devices, such as electrical and electronic parts, mechanical assemblies, optical equipment, and delicate instruments, when contacted with water through cleaning or other processing must be dried promptly to prevent rusting, water staining, and general deterioration that may lower product reliability. A dedicated drying or dewatering process is often used to remove moisture. Typical techniques include: centrifugal or hot-air knife processing followed by hot-air drying; absorbent drying using ethanol, isopropanol, or acetone; vapour drying with non-ozone depleting chlorinated solvents; and displacement drying with PFCs, HCFCs, HFCs, HFEs, chlorinated solvents or hydrocarbons.

8.2.6. Riveting and machining

Machining processes that generate high temperatures, including drilling of deep precision holes, require the significant cooling and lubricant carrying capacity provided by CFC-113. New cutters and high-speed spindles have performed successfully using more traditional non-ozone depleting lubricants such as long chain

fatty alcohols and emulsified water/oil mixtures, sometimes combined with cold air. New lubricant and coolant blends utilizing volatile solvents including HFCs or HFEs are also being introduced that perform in a manner similar to the old CFC-113 blends.

8.2.7. Aircraft Hydraulic Systems

Aircraft hydraulic systems have traditionally been tested by pressurising the systems with hydraulic fluid and looking for leaks. Discovered leaks are stopped and spilled hydraulic fluid is cleaned up, traditionally with CFC-113 and HCFC-141b. The contaminated areas are often large as the fluid flows down from wheel wells and control surfaces often covering large numbers of tubes, components and wiring. Cleaners need to be non-flammable, completely evaporate and possible to flush inaccessible areas without concern for corrosion or other material degradation.

Successful alternatives include testing using inert gas with amplified sound detection of leaks, improving processes to eliminate leaking hydraulic systems, and cleaning up spills with absorbent pads, aqueous cleaners, and HFE and HFC blends.

8.2.8. Leak Detection

Helium gas with mass spectrometry detection is used for leak detection of aircraft fuel tanks, semiconductor housings, etc. As an alternative for CFC-113 immersion of pressurised parts (e.g., gyros), success has been achieved with a blend of cyclic fluorocarbon ether and aliphatic fluorocarbon or with a solution made from pure water and a surfactant. There are also systems available that detect leaks of this type using infrared techniques.

8.2.9. Fabric Protection and Coating

Alternative non-aerosol fabric protection products applied at the mill or by the retailer include hydrocarbon solvents that extend the drying time and are flammable. These products may require additional capital expense to handle and use the solvents safely. One manufacturer has introduced a water-based fluorocarbon resin system that will replace currently used solvent-based fluorocarbon products in this application. The system will require the purchase of special equipment for the application of the water-based product.

8.2.10. Laboratory Testing

CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride are used for analyses in laboratories or investigations (e.g., quality testing and analysing oils and greases). Some uses of ODSs in laboratory applications have been granted a global essential use exemption. However, alternatives have been found for testing of oil, grease, and total petroleum hydrocarbons in water, testing of tar in road paving materials, and forensic finger printing.

8.2.11. Detection of Latent Fingerprints

Several alternatives have been evaluated for the ninhydrin reagent fingerprint detection technique. Some alternatives such as HCFC-141b, HCFC-225, hydrocarbons and alcohols do work, but not as well as CFC-113. The most common

problems have been fading of ink, toxicity, or flammability. Recently, HFC-43-10mee and HFE-7100 have been used with excellent results.

For the 1,8-diazafluoren-9-one (DFO) reagent technique, an azeotrope of HFC-43-10mee with 1,2-trans-DCE and a similar azeotrope of HFE-7100 are being evaluated with some success. The process of fingerprint development with this agent is being optimised to reduce the effect on ink.

8.2.12. Mould Release Agents

New agents for releasing products from moulds include either internal or water-based external release materials. Several manufacturers of aerosol mould release agents have developed "non-solvent" formulations in which the active ingredient is dispensed without the aid of a solvent. However, in some cases, solvent systems are still required and they utilise flammable hydrocarbons or non-ozone depleting chlorinated solvents.

8.2.13. Motion Picture Film Cleaning

Perchloroethylene is a viable substitute for 1,1,1-trichloroethane in virtually all motion picture film cleaning applications. As a result, specially designed cleaning equipment has been developed that limits emissions of perchloroethylene during the cleaning process. Perfluorocarbons, HFCs, HFEs, and HCFC-225 have also been evaluated with success.

8.2.14. Military Applications

For military momentum control gyroscopes and precision guidance instruments to operate reliably for extended periods in harsh environments, contamination-free surfaces are required during fabrication and repair. Possible cleaning alternatives for gyroscopes include non-ozone depleting chlorinated solvents, organic solvents, HFCs, HFEs, HCFCs, aqueous processes, supercritical fluids, and perfluorocarbons.

Hydraulic military vehicle control systems have control valves with extremely small diameter bores as well as parts such as O-ring seals and gaskets made of elastomers. Smaller tactical weapon systems often use a gas control system, in which a source of high-pressure gas controls the actuator system valves. Possible alternatives for hydraulic control system cleaning include alcohols, supercritical fluids, and gas plasma.

8.2.15. Photolithography

Some photoresists used 1,1,1-trichloroethane to develop the image, while other types employ various other non-halogenated solvents and mildly alkaline aqueous solutions. It is possible that no ODS-developing photoresists are manufactured today, but this is not certain and some stocks may exist. Any further phase-out can be easily achieved with materials designed for developers containing an aqueous solution of sodium carbonate or by direct laser etching.

8.3 Alternative Technology Considerations

The selection of the alternative should be based on five primary factors. The alternative:

- Should not be an ozone-depleting substance.
- Should enable the enterprise to maintain a product reliability level at least equal to the past methods.
- Should be economical.
- Should not create significant environmental impact.
- Should not compromise worker or consumer health and safety.

The following hierarchy of alternative classes (in order of most preferred first) has been assembled in consideration of these five primary factors to assist Article 5(1) enterprises with their decision:

1. “No-clean” technology, eliminating the contaminant or changing it so that it does not adversely impact the process or product. (The contaminant may also be changed so that it is easier to remove with non-ozone depleting cleaners.)
2. Aqueous or emulsion cleaning
3. Organic solvent (less toxic than non-ozone depleting conventional halogenated solvents, depending on flammability issues)
4. Fluorinated solvents and blends (HFC, HFE)
5. Non-ozone depleting conventional halogenated solvents (TCE, MC, PCE)
6. Organic solvent cleaning (more toxic than non-ozone depleting conventional halogenated solvents, depending on flammability issues)

Lower level ODSs (HCFC-225, HCFC-141b, n-propyl bromide) may also be considered with the knowledge that they are or may be subject to future phase-out.

8.4 Environmental, Health, and Safety constraints

Perfluorocarbon (PFC) solvents have extremely long atmospheric lifetime and an associated very high global warming potential, so they should only be used in applications where emissions can be kept at or near zero. HCFCs have an ozone-depletion potential and an established phase-out date, which will limit their future use. HFCs and HFEs have high global warming potentials and relatively high cost. Most hydrocarbon and non-halogenated organic solvents are flammable or combustible. It is also important to consider that many alternative solvents are classified as volatile organic compounds (VOCs), which may restrict their emissive use in some geographic areas.

When selecting an alternative solvent, vapour recovery systems may be required to reduce worker exposure and environmental emissions.

Water-based cleaners have a number of characteristics that make them attractive substitutes. Many formulations contain no volatile organic solvents and are non-flammable. They can, however, emit small quantities of hydrocarbons and emulsion-stabilizing substances. In ideal situations, these pollutants can be removed to some extent using, for example, wet scrubbers. Additional energy is sometimes required to heat solutions for effective cleaning performance and to adequately dry parts after cleaning with water-based or low-volatility products.

8.5 Conclusion

These and similar miscellaneous applications generally require specific evaluation of the large variety of alternatives materials and processes available to achieve satisfactory performance without ODSs. However, experience has shown that, with only a few exceptions, it is possible to operate cost effectively without ODSs.

8.6 Sources of Additional Relevant Information

International Workshop on Solvent Substitution

http://www.exchangemonitor.com/dec_scott.pdf

Solvent Substitution Data Systems (US EPA)

<http://es.epa.gov/ssds/ssds.html>

Solvents Discussion Group

http://groups.yahoo.com/group/solvents_group/

The European Solvents Industry Group

<http://www.esig.org/>

The European Chlorinated Solvent Association

<http://www.eurochlor.org/chlorsolvents/generalinfo/info.htm>

Halogenated Solvents Industry Alliance (USA)

<http://www.hsia.org/>

CleanTech Magazine and Annual Exposition

<http://CleanTechCentral.com/>

E-mail addresses of STOC members who can offer advice

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9. Alternatives to ODSs in Developing Countries

Summary

This chapter provides a review of the challenges that the phase-out of ozone-depleting substances is facing in developing countries. CFC-113 (chlorofluorocarbon-113), 1,1,1-trichloroethane (TCA or methyl chloroform), carbon tetrachloride and HCFCs are the ODSs which need to be phased out. Substitutes and alternatives have been identified throughout the world and are generally readily available for incorporation into existing processes. The major drawbacks to the implementation are access to information and knowledge about what are the acceptable alternatives and economic and environmental considerations associated with them.

Details of the technology are adequately addressed in other chapters in this report dealing directly with the alternatives available for each application. Furthermore, there is additional information in previous versions of the Solvents Technical Options Committee Assessment Reports.

The major efforts to complete the transition away from ozone-depleting substances in developing countries are dependent on the areas cited above, namely 1) availability of information, 2) financial and economic needs to assist in the conversions and 3) enforcement of current regulations.

9.1 Introduction

Solvents account for a significant proportion of ozone-depleting emissions. Chemicals targeted for phase-out under the Montreal Protocol include CFC-113 (chlorofluorocarbon-113), 1,1,1-trichloroethane (TCA; methyl chloroform), carbon tetrachloride, and some HCFCs (hydrochlorofluorocarbons). Most of these solvents are used in the manufacture of electronics products, for precision cleaning, to clean metal parts before further processing and as carriers for solvating agents, lubricants, adhesives, and speciality coatings.

Significant progress in achieving the phase-out in developing countries has been made in this sector, given the widespread use of ODSs and the variety and complexity of their applications. Of the various uses, the electronics industry has progressed furthest towards a complete phase-out, in terms of possible alternatives. However, numerous small users, many of whom are undercapitalised, have hampered full phase-out for electronics and metal cleaning applications. In precision cleaning applications, users have been implementing alternatives. Yet, in some cases, they are still searching for solutions for cleaning precision parts that are especially vulnerable to residues or reactions or that have unusually stringent cleanliness criteria.

9.2 Selection of Alternatives

The following substitutes are available worldwide:

- No-clean electronics
- No-clean metal finishing/fabrication/assembly
- Aqueous cleaning
- Hydrocarbon-surfactant cleaning
- Hydrocarbons and derivatives or oxygenated organic solvents

- Trichloroethylene, perchloroethylene, and dichloromethane cleaning
- Halogenated aromatics (monochlorotoluene/benzotrifluorides)
- Hydrochlorofluorocarbons (HCFC-141b, HCFC-225)
- Perfluorocarbons (PFCs) or hydrofluorocarbon (HFCs) and derivatives (PFEs, HFEs)
- Chlorobromomethane or n-propyl bromide
- Volatile methyl siloxanes
- Supercritical fluid cleaning
- Carbon dioxide snow cleaning
- Plasma cleaning
- Ultraviolet/ozone cleaning

The alternatives that may be considered in developing countries should be based on five primary factors. The alternative solvent:

- Should not be an ozone depleting substance,
- Should enable the enterprise to maintain a product reliability level at least equal to the past methods,
- Should be economical,
- Should not create significant environmental problems, and
- Should not compromise worker or consumer health and safety

The alternatives that should be considered for developing countries are:

- "No-clean", keep-clean
- Aqueous/hydrocarbon-surfactant cleaning
- Organic solvent cleaning (with solvents less toxic than non-ozone-depleting halogenated solvents)
- Non-ozone-depleting halogenated solvents (HFC, HFEs, HCFC-225, HCFC-141b)
- PFCs

9.2.1. "No-Clean"

"No-clean" is the recommended option for the manufacture of consumer electronics, and it is a preferred option for the manufacture of more sophisticated printed circuit assemblies, where feasible. To ensure success, however, no-clean processes require skilled operators, increased control of incoming part quality and superior machinery, due to narrow operating windows and time to demonstrate reliability of hardware produced with the technology.

9.2.2. Aqueous/Hydrocarbon-surfactant Cleaning

Some aqueous and hydrocarbon-surfactant cleaning technologies, with proper controls and monitoring, may have low environmental impact due to the low toxicity of the constituents, but this is not always the case. On the other hand, it is necessary to ensure minimal damage when components that are more toxic are used. However, poor housekeeping practices, such as unnecessary dumping of the cleaning tanks, can cause these cleaners to have worse effects than would ordinarily be expected. In addition, if effluent is untreated, cleaning solution, along with any hazardous soils, could cause environmental problems. In an area with problems of water management or water supply, aqueous cleaners may be a poor choice unless efficient water

recycling is possible. Aqueous/hydrocarbon-surfactant formulations should be carefully screened to avoid components that are toxic to humans or cause damage to the environment. The use of aqueous or hydrocarbon-surfactant cleaning should include processes, such as drying, recycling, waste treatment equipment and a proven technology. For metal-cleaning operations, alkaline cleaning often offers economic benefits over the existing solvent processes.

9.2.3. Organic Solvent Cleaning

Although toxicity may be a concern for some formulations, the principal risk is derived from the high flammability of the more volatile compounds and the combustibility of the less volatile ones. Such solvents should not be used in settings with sources of ignition unless appropriate precautions are taken, with proper ventilation and protective equipment. Similarly, the possibility of soil or groundwater contamination is of concern if proper materials-handling practices are not followed. Caution should be used when these solvents are employed with sprays, heaters, or ultrasonic equipment.

9.2.4. Non-ozone-depleting Halogenated Solvents

Where emission issues are of concern, emission control equipment should be included to meet domestic regulations. Strict adherence to proper industrial hygiene practices is essential where these solvents are used because of their often-low operator exposure limits (OEL). These chemicals have properties that may cause human health and environmental problems. However, new equipment, although expensive, is available that can control emissions and therefore reduce the risks. If poor attention to equipment maintenance, chemical handling and waste disposal procedures is possible, these chemicals should generally be avoided, since spills can lead to unacceptable worker exposure and soil or groundwater contamination. All of these chemicals are associated with high start-up costs due to expensive equipment. On the other hand, non-ozone-depleting halogenated solvents may offer the lowest operating costs, in some cases, since some solvents are among the least costly chemicals. However, there is a high risk of contaminating soil and/or groundwater in spite of well-engineered and maintained systems. See Appendix 2 for further details.

9.2.5. HCFC-225, HCFC-141b, HCFs and HFEs and PFCs

HCFC-225 is very similar to CFC-113 in physical and chemical properties, and can form azeotropes with alcohols. It exhibits good materials compatibility and can therefore be used to replace CFC-113 with few changes in the process. HCFC-225 has been used in applications where other alternative technologies cannot be applied, despite its relatively high cost.

Because of its high ozone-depletion potential, HCFC-141b is never suitable as a substitute for 1,1,1-trichloroethane. It is suitable as a substitute for CFC-113 only when lower ozone-depleting potential alternatives, including HCFC-225, are not feasible. Because HCFCs are transitional in nature, a second shift to a non-ozone depleting alternative will ultimately be required. It may be more cost effective to move immediately to a non-ozone depleting technology to avoid the costs associated with qualifying and changing the cleaning process twice, if possible.

HFCs and HFEs are relatively low-solvency substitutes for CFC-113 and they have no known ozone-depletion potential. They do have a high GWP and HFCs are controlled under the Kyoto Protocol. They are currently recommended only for applications

where it can be proved that no other non-ozone depleting potential product or method can be used.

PFCs should only be used in electronics and precision cleaning applications where no other alternative will provide the needed performance. Low emission equipment is available for PFCs. PFCs have a very high GWP and are controlled under the Kyoto Protocol. PFCs are not likely to be an acceptable substitute for manufacturing processes in developing countries, especially as they are extremely expensive. HFCs, HFEs and VMSs are expensive and should be considered only where they are cost-effective and essential because of compatibility, toxicity, and safety.

9.2.6. Other solvents and processes

Use of practices and local environment considerations can move a particular chemical either up or down in the selection hierarchy. Supercritical fluid cleaning (SCF), plasma cleaning and ultraviolet ozone cleaning are recommended for use and financing if they can be shown to be the only technical solution and are cost effective. Even though they have low environmental impact, they are mostly used for speciality applications because of dedicated engineering and training requirements. Other emerging technologies, such as brominated solvents, are not recommended for implementation and financing until they are developed further.

9.3 Environmental, Health, and Safety Constraints and Retrofits

Health and environmental aspects should be considered prior to selecting alternative processes and technologies. For current users of CFC-113, carbon tetrachloride, or 1,1,1-trichloroethane solvents as cleaners, the most likely retrofits are as follows:

9.3.1. Chlorinated Solvents

Retrofitting existing equipment for chlorinated solvents is generally possible at relatively low cost. The chemical properties of these solvents are similar to 1,1,1-trichloroethane and CTC and the costs minimal. Most modern equipment can be modified to use any other chlorinated solvent and meet prevailing national standards. However, modifications can be expensive and more difficult to meet the operator exposure, volatile organic compound (VOC) and air quality requirements. The U.S. Maximum Achievable Control Technology (MACT) standards will require more investment in equipment retrofit than the OSHA standards. If periodic monitoring, record keeping, and reporting are required, this can add to the cost. It is essential to add solvent spill containment and recovery in all places where these products are used or stored. The cost of the retrofit should include a period of monitoring the vapour emissions from the machine, and take into account the costs associated with cleaning up contaminated soil and/or groundwater. In addition, monitoring on a basis that is possible in industrialised countries may be difficult to put into practice in some developing countries.

9.3.2. HCFC-225

Since the physical and chemical properties of HCFC-225 are similar to CFC-113, this solvent can be used in a retrofit application to modern machines, but it is recommended only for applications where other, more environmentally acceptable alternatives, are not feasible. Due to the relatively high cost of HCFC-225, its lower Operator Exposure Limit and the fact that it is ozone depleting, low loss equipment, which is now commercially available, is recommended. Note that the cost of

retrofitting or replacing the existing machines may not necessarily be written off before this solvent too, must be phased out under the Montreal Protocol.

9.3.3. HCFC-141b

Due to a lower boiling point and high ozone-depletion potential of HCFC-141b, a retrofit can be expensive. Extensive degreaser modifications must be made, such as adding freeboard, chillers, programmable hoists, automatic sliding access ports, and molecular sieves in order to reduce emissions. Moderately high retrofit costs, combined with higher chemical costs, make HCFC-141b a poor candidate for retrofits and is not recommended for investment. As it is currently being phased out in some developed countries, continuation of manufacturing the solvent cannot be guaranteed from those sources.

9.4 Conversion of Equipment From Solvent to Aqueous Technologies

Retrofits to aqueous and hydrocarbon-surfactant cleaning is also possible. Degreaser tanks are sometimes retrofitted for water based cleaners, but this requires extensive engineering design and should not be attempted without direct consultation with a qualified equipment supplier. For hydrocarbon-surfactant processes also, the chemical manufacturer must be consulted.

9.5 A Profile of Phase-out Strategy

The strategy for phasing out ozone depleting solvents is unique for each of the Article 5(1) countries and for the individual enterprise within the country. A large number of factors including the quantities and pattern of use in various industrial sectors profoundly influence the policies. However, some aspects of planning and execution are generic in nature and form an integral part of any such strategy. For example, identification of controlled solvents in use, estimation of current consumption, future projections, availability of suitable alternatives, economic implications etc. should form an integral part of planning. Hence, the components for developing a strategy may include the following:

- Identification of specific applications/processes which use ODSs, e.g., electronics, precision and metal cleaning etc.
- Analysis of data on manufacture and imports of controlled solvents
- Evaluation of substitutes and alternative technologies
- Assessment of awareness of industry with respect to implementation of the Montreal Protocol
- Assessment of incremental costs of phase-out as per the available international norms
- Resource planning for phase-out targets for a given solvent/industrial sub-sector
- Formulation of the most appropriate methodology to effectively phase-out the ODSs without affecting industrial production and economic growth
- Regulatory regime to control manufacture and/or imports of controlled solvents
- Development of an implementation plan

The schedule of implementation of a phase-out programme in all the Article 5(1) countries has been drawn up and the target dates for each controlled solvent have been

specified. Keeping these targets in view, each Article 5(1) country is expected to formulate a country-specific plan based on its resources. Among the tasks the Article 5(1) countries must manage efficiently, the most significant ones are:

- Cost estimates for implementation phase
- Solvent specific phase-out target years
- Establishment of technology support systems to cater for the respective industry sectors
- Establishment of demonstration centres or other means for providing hands-on experience to the industrial units
- Conception of a Health, Safety and Environment Programme to applicable/accepted norms
- Special endeavours for providing financial and managerial assistance by involving NOUs and Implementing Agencies

9.6 Multilateral Fund

The funding of Article 5(1) projects in the Solvents Sector has proved more difficult than in some other Sectors. This is shown by the small number of completed projects, compared with the number of OD solvents users. There are many reasons for this situation, including:

- Difficulty in identifying potential projects
- The average solvents user may purchase only a few OD tonnes annually. This means that the funding that would theoretically become available would be too small to permit the purchase of capital equipment.
- The Implementing Agencies would be insufficiently remunerated to consider small projects.
- Umbrella projects rarely prove successful, because each beneficiary has individual requirements
- New projects often show incremental operating cost (IOC) savings, even with large users, which would partially or totally wipe out the funding available for capital equipment, based on the cost-effectiveness threshold. This has sometimes resulted in the beneficiaries opting for expensive technologies, with no IOC savings, rather than the more obvious low-cost one.
- Many potential projects fail because of the unavailability of or the unwillingness to provide counterpart funding.
- Fear of the use of some solvent types that may require E., H&S precautions (often this fear is unfounded)
- Some projects have initially been poorly engineered, requiring long and expensive corrections and delays
- Many potential projects may be suitable for replacing the OD solvent with a “no-clean” technology, where implementation costs are negligible. Where the user has the necessary technical knowledge, he may implement this without funding; this has already been done in many cases, without it being officially recorded. Where the user does not have access to the knowledge, the implementation is usually not achieved.
- Many large users who are subsidiaries of or otherwise related to companies in developed countries may be funded by their principals and do not seek MLF grants.

Another observation is that many users, who have phased out the use of OD solvents, ignore even the most basic E, H&S precautions.

The STOC cannot make recommendations to improve the number or scope of funded projects, but mentions these problems to allow future projects to avoid some of the pitfalls.

9.7 Guidelines for SMUs in Developing Countries

The situation regarding small and medium users in Article 5(1) countries is particularly difficult. Government authorities may find it impossible to identify them and, even if they do, they are likely to meet more resistance to change because the users simply do not understand the situation. It is also frequently impossible to follow the complex supply chain of manufacturers, importers, distributors, blenders, wholesalers, and retailers.

As a rule, the technical “know-how” regarding solvents in many SMUs requires updating, and, if a supply is stopped, the user may not know whether a suitable alternative is available. This lack of knowledge is exacerbated by a frequent non-availability of good, concise technical information in the local language.

NOUs may find it useful to put advertisements in national and local newspapers offering, free-of-charge and with no further liability, such translated documents, with a heading of the controlled solvents, their more popular local names and applications. At the bottom, a voluntary contact name and address should offer further help.

The crux of the matter is that most SMUs will have to fend for themselves, as soon as supplies of OD solvents dry up. In many cases, this will cause economic hardship or may even force some enterprises to close. Unfortunately, there is no easy answer. Individual governments may be able to provide a partial answer by global sectorial phase-out plans, but these are very unlikely to reach the smaller production units for the reasons stated, especially if they are geographically remote from the regional centres. The best that can be done is for governments to provide funding, where the MLF cannot.

9.8 Conclusions

The choice of the “no-clean” option should be the preferred substitution strategy. However, this option requires skilled operators, control of incoming part quality and appropriate machinery to insure the reliability of the products. Where aqueous or hydrocarbon/surfactant cleaning is employed, it is important to consider aspects related to environment, health and safety of workers. Financing of projects by the Multilateral Fund should include pollution prevention, recycling, waste water treatment, and drying equipment, as appropriate. It must also include containment equipment, adequate ventilation control, and/or low emission equipment and should provide for cost of monitoring these projects.

Development of a comprehensive strategy for phasing out the ODSs warrants a reasonable understanding of their applications and the most appropriate alternative for each. Resource planning and a schedule for implementation of a regulatory regime are some of the most important aspects that need to be considered.

For SMUs, the phase-out is likely to be difficult, primarily because of a lack of organisation and awareness of its importance. An additional major challenge is accessing good information about available alternatives.

9.9 Contact addresses for further information

Solvents users should initially contact their local National Ozone Unit. This is generally a department of the Ministry or Department of the Environment, depending on the national organisation.

STOC members with particular knowledge of Article 5(1) country problems are:

aakhan_iict@rediffmail.com / aakhan777@yahoo.co.uk

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A.1. Appendix 1. The n-Propyl Bromide Situation

Summary

The situation regarding n-propyl bromide (nPB, 1-bromopropane) remains unclear because its effect on the ozone layer and its chronic toxicity are still unknown. These issues are being researched but no definitive results are likely for some time.

At the time of writing, the ozone-depleting potential of nPB is still unknown but the Scientific Assessment Panel is working on the development of a model that will assess how emissions will damage the ozone layer over a period of time. Results from this study are expected in 2003.

The chronic toxicity of nPB is still unknown, but there are anecdotal reports of neurological disorders in humans, resulting from exposure to nPB. Animal testing is unlikely to be completed before the end of 2003, at the earliest.

World production capacity for the manufacture of nPB is increasing, although the consumption is currently stable. This is resulting in a lowering of bulk prices, to a level comparable to the upper limit of chlorinated solvents.

The regulatory climate for nPB is showing signs of becoming more severe.

It is the STOC's opinion that nPB may be useful for a few niche applications but, in our current state of knowledge, it should be used only under the following conditions:

- That no non-ozone-depleting solvent or process can be used for the application.
- That atmospheric emission is reduced to as near zero as possible (this may imply that only expensive "zero-emission" machinery should be used), to reduce potential damage to the ozone layer to a minimum.
- That operator exposure be reduced to as low a level as is technically feasible and prolonged exposure levels monitored.
- That users be aware that future regulations may severely control or prohibit the use of nPB because of either ozone-depletion or toxicity concerns.

Introduction

The situation regarding n-propyl bromide (nPB, 1-bromopropane) remains unclear because its effect on the ozone layer and its chronic toxicity are still unknown. These issues are being researched but no definitive results are likely for some time.

Solvent blends based on nPB have characteristics similar to carbon tetrachloride, trichloroethylene, 1,1,1-trichloroethane and HCFC-141b. As such, it may be a potential substitute for all of these.

An *ad hoc* Task Force of TEAP, at the request of the Parties to the Montreal Protocol, reported their findings in 2001 and their report can be downloaded at <http://www.protonique.com/unepstoc/report/nPBReport.pdf>. This was followed by a shorter update report in 2002, incorporated in the TEAP Progress Report at <http://www.teap.org/REPORTS/downloads/TEAP02V1.pdf>. As a result of these, the Parties have recommended the adoption of the precautionary principle in Decision

XIII/7, where use of this solvent seems desirable, notably to reduce emissions to a minimum and to ensure that operators have minimal exposure to the substance.

Ozone Depletion Potential

The classical models cannot determine the ozone-depleting potential of nPB because it has a short atmospheric residence time (lifetime) and because some of the decomposition products may have a higher ozone-depleting potential than the substance itself. Furthermore, because mixing in the atmosphere is incomplete, the transport of the bromine-containing molecules to the ozone layer depends on different mechanisms than substances with a long lifetime. These mechanisms are dependent on a number of variables including the place of emission (notably the latitude), the weather, the season etc. As a rough rule of thumb, the closer the place of emission is to the tropics, the higher will be the resultant depletion of the ozone layer for a given quantity emitted. Various estimates have been made of the ozone depleting potential by modifying the classical models but the results have been somewhat inconsistent. These vary within a low range at high latitudes, to typically about 0.01 to 0.05 at mid-latitudes, up to 0.08 to 0.15 within the tropics. These values are comparable to the ozone-depleting potential of some controlled substances.

At the time of writing, the Scientific Assessment Panel is working on the development of a model that will not so much give an ozone-depleting potential value as to assess how emissions will damage the ozone layer over a period of time. Results from this study are expected in 2003.

Toxicity

The acute toxicity of nPB is reasonably low and normal worker exposure should not present a short-term problem.

Sub-chronic toxicity testing reveals that the substance may cause reproductive and neurological disorders at moderate operator exposure levels. Studies on animals have shown that it would be wise to adopt quite low operator exposure levels. Most serious manufacturers recommend Time-weighted Average (TWA) levels over 8 hours per day, 5 days per week, of 5 to 25 ppm, although some makers may recommend up to 100 ppm. No official values have yet been issued, pending the results of chronic toxicity testing.

Chronic toxicity testing is not likely to be completed, and the results known, before late 2003, at the earliest.

No epidemiological studies on humans have been presented. However, anecdotal reports have mentioned severe neuropathic problems in a small number of operators. Further information is needed to determine if the effects on humans and their sensitivity differ from that of animals.

For reasons of the doubt regarding toxicity, it would be a wise precaution to ensure that operator exposure through inhalation and dermal uptake were minimised to a level consistent with a toxic substance.

Production and Consumption

nPB is produced in a number of Article 5(1) and non-Article 5(1) countries. Current global production is estimated at between 5,000 and 10,000 tonnes per year, but

production capacity has recently been increased by a further 12,000 tonnes per year, with a new Chinese factory coming on line. Total current capacity is probably in the region of 25,000 tonnes per year. This could be easily increased to meet any future demand.

Estimates of likely future global annual consumption within a decade, assuming no regulatory barriers, are about 60,000 tonnes. Less likely, but possible, “upper bound” estimates reach about 250,000 tonnes per year, but only if nPB replaces the majority of non-ozone-depleting chlorinated solvents in cleaning applications.

Price

At the time of publication of the 2001 TEAP report, the range of price of nPB was estimated at USD 3.00 to 5.00/kg in bulk quantities. The latest information, derived from e-mailed publicity from a Chinese company, quotes a solvent-grade, CIF European Port, cost of USD 1.72/kg. This reduction, possibly resulting from increased competition due to new capacity coming on line, brings the price down to a level equivalent to the top of the range for common chlorinated solvents. If there are no regulatory influences due to ozone-depleting potential or toxicity, this could mean an accelerated replacement of chlorinated or other solvents, in those countries that have severe regulations governing the latter.

Regulations

In view of the possible toxicity issues, the UK have proposed to the European Union that nPB be subjected to very severe labelling requirements, warning users of potential dangers. The French Institut National de Recherche et de Sécurité (INRS) has published (in French) severe warnings about exposure to nPB at

http://www.inrs.fr/cgi-bin/searchmeta/search_querynf.pl?keywords=npb&words=all

Conclusion

The STOC emphasises the precautionary principle proposed by the Parties to the Montreal Protocol in Decision XIII/7. It is of the opinion that nPB may be useful for a few niche applications but, in our current state of knowledge, it should be used only under the following conditions:

- That no non-ozone-depleting solvent or process can be used for the application.
- That atmospheric emissions be reduced to as near zero as possible (this may imply that only expensive “zero-emission” machinery should be used), to reduce potential damage to the ozone layer to a minimum.
- That operator exposure (including dermal uptake) be reduced to as low a level as is technically feasible.
- That users be aware that future regulations may severely control or prohibit the use of nPB because of either ozone-depletion or toxicity concerns.

Relevant Information

<http://www.teap.org/REPORTS/downloads/>

e-mail addresses of STOC members who can offer advice

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A.2. Appendix 2. The Proper Use of Halogenated Solvents

Foreword

This appendix was written by the TEAP and STOC to provide guidance as to how common halogenated solvents may be used. It has been reproduced as originally written but with modifications to the formatting to be consistent with the rest of this report.

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Introduction

Users of ODSs are frequently perplexed with the choice of possible alternative solvents and cleaning methods. In some cases, the only technically or economically viable options are the use of chlorocarbon or halogenated solvents. The non-ozone-depleting chlorocarbon solvents are usually trichloroethylene, perchloroethylene, or methylene chloride. These hazardous solvents can be used safely, if precautions are taken. Trichloroethylene, perchloroethylene or methylene chloride solvents are less costly than other halogenated solvents, in many cases. They are more toxic than hydrofluorocarbons but less toxic than the majority of bromocarbons.

The purpose of this document is to enable users to determine whether low-cost chlorinated solvents may be safely used, especially in Article 5(1) countries, either as a permanent or an interim measure. Advice is given as to how best to implement their use and the precautions required.

Choice of Solvents

In the STOC assessment reports [STOC, 1994, 1998], a preferred hierarchy of the main ways of replacing ODSs for cleaning applications has been stated:

- "No-clean"
- Water cleaning
- Saponifier or detergent cleaning
- Hydrocarbon-surfactant cleaning ("semi-aqueous")
- Hydrocarbon solvent cleaning (where the toxicity is lower than halocarbons)
- Halocarbon solvent cleaning
- Hydrocarbon solvent cleaning (where the toxicity is higher than halocarbons).

*This document in no way changes the preferred hierarchy. Halocarbon solvent cleaning, along with the use of toxic hydrocarbons, are the **least preferred** options.*

Classes of Halocarbon Solvents

A halocarbon solvent is one containing one or more halogen atoms in an organic molecule. There are four main types of halogens:

- Fluorine
- Chlorine
- Bromine
- Iodine.

Solvents containing chlorine or bromine may be ozone depleting. Solvents containing only fluorine or iodine are generally not ozone depleting. However, solvents containing fluorine and chlorine or bromine usually are ozone depleting. Six main solvents are controlled under the Montreal Protocol:

- Carbon tetrachloride
- 1,1,1-trichloroethane
- CFC-113
- HCFC-141b
- HCFC-225
- Chlorobromomethane (also known as bromochloromethane)

In addition, parties to the Protocol discourage the use of n-propyl bromide (nPB), pending final determination of its impact on the ozone layer and out of concern that it may be highly toxic.

There are also three commonly used, low-cost, chlorocarbon solvents whose ozone-depleting potentials are so low that they are not included in the Montreal Protocol:

- Trichloroethylene
- Perchloroethylene
- Methylene chloride.

A number of specialised solvents are also being marketed, such as hydrofluorocarbons (HFCs), oxygenated derivatives of them (hydrofluoroethers and hydrofluoroketones), polyfluorocarbons (PFCs), hydrofluoropolyethers (HFPEs) etc. These all have zero ozone-depleting potential but some of them have high global warming potentials. As a rule, they are not very good for many contaminants but blends of them with other solvents provide characteristics that are very useful in some applications. They are all expensive and, as such, their use is limited to applications where their unique characteristics are required. They therefore fall out of the scope of this document.

Carbon Tetrachloride (CTC)

Synonyms: tetrachloromethane.

Carbon tetrachloride is a very effective chlorinated solvent. It is stable, which, combined with the fact that it has all its hydrogen atoms replaced by chlorine ones (perchlorinated), is the reason that it is ozone depleting. Its ozone-depleting potential is the highest of all the common solvents (1.1). It is very toxic and is possibly carcinogenic to humans. For this reason, its use was abandoned as a solvent in most developed countries in the 1950s. It was first discovered in 1839 and became popular for metal degreasing from the late 1890s and as a dry cleaning solvent (to replace flammable solvents) in the 1930s, until it was replaced by perchloroethylene in the late 1950s. It is the cheapest of all chlorocarbon solvents.

1,1,1-trichloroethane (TCA)

Synonyms: methyl chloroform.

Between 1950 and 1980, 1,1,1-trichloroethane became popular to replace other chlorocarbons because of its lower toxicity. It has a relatively low ozone-depleting potential (0.1) but it has significant impact on the ozone layer because of the sheer volume used. It was used initially as a cold-cleaning solvent but, as stabilisers were developed, it also became the leading solvent for vapour-phase cleaning. It is also used as a solvent for some classes of adhesives. Its price was moderately low, but slightly higher than all the other chlorinated solvents. Besides metal cleaning, it was also popular for dry cleaning in the Far East and Japan.

CFC-113

Synonyms: 1,1,2-trichlorotrifluoroethane

CFC-113 is a milder solvent than CTC and TCA. It has a high ozone-depleting potential (0.8). Its main applications were for defluxing electronics assemblies and for precision cleaning, although it has also been used as a niche solvent for other

purposes. It has a very low toxicity. It was also used as a speciality dry cleaner for some delicate fabrics and special garnitures. Its price is high compared with chlorocarbon solvents.

Chlorobromomethane (CBM)

Synonyms: bromochloromethane

Chlorobromomethane has a similar solvency to 1,1,1-TCA. It is toxic and ozone depleting (value > 0.1). It was employed briefly in the mid-1990s for degreasing metals in vapour-phase degreasers, but its unacceptable ozone-depleting potential and toxicity caused it to be controlled by the MP.

Trichloroethylene (TCE)

Synonyms: 1,1,2-trichloroethene, Tri, Trichlor.

Trichloroethylene has been used as a popular degreaser since 1908. Current world production is about 545,000 tonnes per year, of which about 39% is used for metal cleaning. Its main application was, and still is, for metal cleaning, although it has been used for dry cleaning and for chemical extraction of, e.g., to remove caffeine from coffee beans. As a metal cleaner, it can be used either as a cold cleaner or in a vapour-phase degreaser. It has very similar characteristics to CTC and TCA and generally can substitute for either in most cleaning applications with very little modification to either process or equipment. It is moderately toxic and must be used under controlled conditions. It is inexpensive, only slightly higher in price than CTC.

Perchloroethylene (PCE)

Synonyms: tetrachloroethylene.

Perchloroethylene has been manufactured commercially since 1910. Current world production is about 630,000 tonnes per year. About 25 per cent of this is used for dry cleaning and 19 per cent in metal cleaning. It is the main and preferred solvent used for dry cleaning, since the 1950s. It is also widely used for metal cleaning, especially in parts of Europe in vapour degreasers. Its higher boiling point than that of TCE offers advantages for removing heavy greases. It is moderately toxic and must be used under controlled conditions. It is inexpensive, only slightly higher in price than TCE.

Methylene Chloride (MC)

Synonyms: dichloromethane

Methylene chloride has been widely used as a component of paint, photoresist, and wire strippers, as a diluent for some adhesives and for metal cleaning, for many years. Current world production is about 450,000 tonnes per year. Some 40 per cent of this is used in strippers, 6 per cent for metal cleaning, and most of the remainder as diluents for adhesives, paints and similar applications. It has a lower boiling point (c. 40 °C) and a lower vapour density, making it more volatile than other chlorinated solvents. It is moderately toxic and must be used under controlled conditions. It is inexpensive, slightly lower in price than TCE.

n-Propyl Bromide (nPB)

Synonyms: 1-bromopropane, *normal*-propyl bromide

n-Propyl bromide is a relatively new solvent, although the molecule has been used by the pharmaceutical industry for many years. It has characteristics very similar to CTC, TCA, and TCE and can be used interchangeably with these in many cleaning applications. It is also used as a diluent for some adhesives, as a replacement for methylene chloride. The Scientific Assessment Panel is investigating its ozone-depleting potential. It is suspected to be so toxic that some chemical companies have recommended very low worker exposure limits and other companies have halted production and marketing for solvents applications. Appropriate authorities have not yet announced definitive toxicity tests results. It is more expensive to manufacture than all the above solvents except CFC-113.

Toxicity of Halogenated Solvents

All halogenated solvents are toxic by any means of absorption. Their toxicity is variable and must be classed according to the exposure path, the exposure time, and concentration. For the sake of this document, it will be assumed that dermal absorption can be avoided by the use of suitable gloves, goggles, and other personal protection equipment, which are mandatory with all solvents. Care should be taken to avoid solvents entering into gloves or other protective clothing, because the occlusion will accelerate dermal uptake. It is also assumed that operators will not drink the solvents (avoid using drink bottles for storing them!). This leaves inhalation. A distinction should be made between acute and chronic toxicity. Acute toxicity is that produced by a single, short, exposure at a high level. The acute toxicity of all these solvents is relatively low, although very high exposure levels can be dangerous. Chronic toxicity is manifested during normal daily exposure to fairly low levels of solvent vapours. It is usually expressed in parts per million (ppm) of the time-weighted average exposure to the solvent in air, often with a short term ceiling value. These values vary according to the regulatory authorities in each country and may be expressed by a number of different terms, such as permitted exposure level (PEL), threshold limit value (TLV), maximum Arbeitsplatz Konzentration (MAK) and so on (or their respective abbreviations). These are usually defined as the time-weighted average (TWA) of 8 hours exposure per day, 5 days per week. In this document, the terms “operator exposure level” (OEL) and “ceiling exposure level” (CEL) will be used to include all these. The CELs also include a maximum time scale, usually 15 or 30 minutes.

The following table shows the ranges of known OELs and CELs permitted or recommended for the major solvents in different countries (please note that the ranges of values may not be exhaustive):

Appendix 2, table 1: Ranges of Known OELs and CELs

Solvent	OEL ppm	CEL ppm	Guideline OEL ppm ¹	Regulated Under MP
CTC	2-10	10	3	Y
TCA	250-500	450	250	Y
CFC-113	500-1000	1250	850	Y
HCFC-141b	200-500		250	Y
HCFC-225 ²	50		50	Y
CBM	100-200		<5	Y
TCE ³	5-100	1.9-300	50	N
PCE	10-100	1.5-300	50	N
MC	5-100	14-500	40	N
nPB	5-100		<20	N

The following table shows the OELs and CELs, for the non-ozone-depleting chlorinated solvents, of individual countries and states, where the values are known. These values are given in good faith and no guarantee can be given as to their accuracy. In general, the OELs are TWA values for 8 hours per day, 5 days per week, although minor variations may exist. The CEL specifications are much more variable, regarding the permitted time of exposure.

¹ The guideline OEL is unofficial and is not intended to replace official national values. It may be used as a gauge where there is no official value or where the official value is higher, for additional safety. It represents TWA values that are considered by experts to be safe for worker exposure for 8 hours per day, 5 days per week, or less. For longer exposure times, it may be judicious to reduce the OEL. A guideline ceiling value can generally be considered as twice the OEL for a maximum of one 30-minute period per week, on condition that the TWA does not exceed the OEL.

² Mixture of ca and cb isomers

³ Note that Germany considers that TCE is carcinogenic to humans, although this has not been proven. In that country, and any others following the German MAK regulations, the OEL is set at 50 ppm. This apparent contradiction is because it is considered that no cellular changes take place below a given threshold level. In contrast, Germany has the highest OEL for CTC (10 ppm), compared with 2 ppm for France and 5 ppm for the USA, where there are more reasonable grounds for suspecting CTC to be carcinogenic.

Appendix 2, table 2: OELs and CELs for Non-ozone-Depleting Chlorinated Solvents (ppm)

Jurisdiction	Perchloroethylene		Methylene Chloride		Trichloroethylene	
	OEL	CEL*	OEL	CEL*	OEL	CEL*
Alberta	50	100	50	200	50	200
Argentina	50	200	50		50	200
Australia	50	150	50		50	200
Belgium	25	100	50		50	100
Brazil	78		156		78	
China	30**		58**		5.6**	
France	50		50	100	75	200
Germany	50	200	100	400	50	200
Hong Kong	25	100	50		50	100
India					50	200
Italy	25	100			50	100
Korea (North)					5	
Korea (South)	50	200	50		50	200
Malaysia	25		50		50	
Manitoba	25	100	50		50	100
Mexico	100	200	100	500	100	200
Netherlands	35		100	500	35	100
New Zealand	50	150	50		50	200
Ontario	25	100	50		50	200
Phillipines	100		500		100	
Quebec	50	200	50		50	200
Russia		1.5		14		1.9
Singapore	25	100	50		50	100
Spain	25	100	50		50	100
Sweden	10	25	35	70	10	25
Taiwan	50		50		50	
Thailand	100	300			100	300
United Kingdom	50	100	100		100	150
USA***	100		25	125	100	

Notes:

* Conditions for CEL vary from country-to-country (see text)

** Recommended values only

*** These are the legal federal OSHA PEL limits. State or recommended limits from other authorities may be different.

Carcinogenicity

No halogenated solvent has been shown to be carcinogenic to humans, according to the strictest rules of toxicology and epidemiology, although there is some doubt regarding carbon tetrachloride. Many cohort studies for TCE, PCE, and MC, involving thousands of workers exposed to these substances over decades of work, have revealed no significant evidence of an increase in the risk of cancer of any type, or an overall increase of any specific type of cancer. It should not be forgotten that some of these

solvents have been widely used in industry, often under bad exposure conditions by modern standards, for over 90 years, so a large backlog of experience has been gained. With the possible single exception of CTC (and even this is not certain), no reliable cases of undue cancer have been observed amongst workers.

One case has been widely quoted and has been used in Germany for establishing draconian exposure limits for trichloroethylene. However, this case had severe confounding factors, which render the results unreliable. It took place in a cardboard/carton factory in E. Germany before the reunification. TCE was widely used under uncontrolled conditions. A small number of workers, but more than would have been statistically likely, did develop cancers. The TCE was blamed for this, although there were four significant confounding factors in the study that were not taken into account:

- Other chemicals used in the same factory under bad conditions
- The probability that the TCE was stabilised with an epoxide substance (epichlorohydrin), which is a strongly suspected carcinogen and is generally no longer used as a stabiliser
- The personal habits (e.g., tobacco and alcohol) of the cancer patients.
- This was a pre-recognised cluster of cases and thus the study is "hypothesis setting" and not proof of a relationship. Large, well-conducted, cohort studies do not support the relationship.

These, combined with the small cohort, have led epidemiologists to conclude that no reliable evidence exists from this isolated case.

The European Centre for Toxicology and Ecotoxicology has published a series of reports describing detailed studies for trichloroethylene [ECETOC, 1994], perchloroethylene [ECETOC, 1990, 1999] and methylene chloride [ECETOC, 1988, 1989,]. These were all written by committees of experts and peer reviewed by groups of further experts in the fields of toxicology and epidemiology. These have all concluded that there is no evidence of any of these three solvents being carcinogenic to humans at exposure levels consistent with modern practice in Industry. There is evidence that they may be carcinogenic in high doses to laboratory animals whose metabolism is totally different from that of the human species. It would therefore be unwise to extrapolate the effect on rodents to humans. It should be noted, however, that all three of these solvents are otherwise toxic and reasonable operator exposure levels should be respected, in order to protect the health and safety of the operators. As a rule, these operator exposure levels are calculated with a very large safety margin (usually 10:1) below the lowest known value where a negative effect may be encountered.

Similar conclusions are drawn by the U.S. Halogenated Solvents Industry Alliance (HSIA) in a number of white papers, although these are tempered by the regulatory climate in the USA. These refer to trichloroethylene [HSIA, 2001], perchloroethylene [HSIA, 1999] and methylene chloride [HSIA, 1994]. Note that these papers, unlike the ECETOC ones, are not scientific studies in themselves but rather a synthesis of conclusions drawn from a number of such studies. They can be downloaded from http://www.hsia.org/white_papers/paper.html

The US EPA Science Advisory Board confirms that the preponderance of evidence for trichloroethylene does not advocate classification as a probable human carcinogen (Category B2) under the Agency's 1986 guidelines for carcinogen risk assessment, and

that the uncertainties and moderate nature of the responses should be emphasised. The solvent is being reassessed under revised guidelines proposed in April 1996. The revised guidelines provide for greater use of mechanistic data to account for differences in response between test animals and humans observed after exposure to substances like trichloroethylene.

Sensible precautions are sufficient to ensure that the operator exposure levels are never exceeded during normal operation of cleaning equipment. These are described later in this document.

Volatile Organic Compounds (VOCs)

All organic solvents are VOCs, by definition. Both the USA and the European Union define VOCs, from the legal standpoint, rather arbitrarily.

From the environmental point of view, a VOC is a substance whose vapours react with nitrogen oxides, in the presence of sunlight, to form tropospheric ozone. This ozone, if the concentration is sufficient, can cause distress and illness in humans and other species. It is also a precursor of "smog" which can often be observed in large cities, especially in the tropics or sub-tropics. This smog is harmful and may be responsible for a massive increase of pulmonary conditions in some regions. It is therefore important to minimise emissions of solvents (and other products) that may contribute to an important increase of VOC levels, especially in urban communities.

Existing legislation does not take into account that different solvents have very widely different effects in the production of photolytic ozone, nor that the latter also requires NO_x to be generated. Nor does it consider the effect of the operational vapour pressure (for example, a solvent with a very low vapour pressure at ambient temperature may not be legally a VOC, even though it is always used at an elevated temperature, at which reactive emissions may be considerable). European legislation gives some exemptions for small users, below a given use threshold. However, this threshold and the quantity of emissions permitted vary between applications. For example, for dry cleaning of clothes, the limit of solvents emitted, irrespective of the type, is 20 g/kg of dry weight of cleaned garments, whereas shoe manufacturers are permitted to emit 25 g per pair, while solvent cleaning of surfaces is permitted to have fugitive emissions between 10 and 20 per cent of their solvent input. Yet, all of these applications may be using the same solvent. The point that is being made here is that it is not appropriate to assume that, because legislation exists in some countries, it is applicable without further thought to other countries.

It is useful to note that European regulations also fix stack emissions of solvent vapours. This is the proportion of solvent vapours to be found in ventilation stacks from the factory and, for large users, is fixed at very low permissible values. This must not be confused with the OEL.

The real question is whether non-ozone depleting chlorocarbon solvents are VOCs. The answer is positive, but with qualifications. Perchloroethylene and methylene chloride have a very low photolytic reactivity to form tropospheric ozone or smog, compared with most non-chlorinated organic solvents. It can therefore be categorically stated that, if emissions are limited to reduce workplace exposure, it is unlikely that they will make a significant contribution to ozone formation. Trichloroethylene, on the other hand, has reactivity about double that of the other chlorinated substances and

restrictions on emissions may be desirable in urban locations where pollution is a problem, although it is still very small.

The following table has been adapted from one at:

http://www.eurochlor.org/chlorsolvents/issues/issues1_2_2.htm#environment.

Appendix 2, table 3

	Tropospheric Ozone Creation Potential
Ethylene	1.0
Xylenes	0.8 to 1.1
Methyl-ethyl-ketone (MEK)	0.51
1,1,1-Trichloroethane	0.002
Trichloroethylene	0.075
Perchloroethylene	0.035
Methylene chloride	0.031

Global Warming Potential (GWP)

All solvents have a global warming potential. This is usually some form of function of the residence time of the solvent vapours. Generally, the more stable the solvent, the higher the GWP.

The following table, derived from numerous sources, indicates that the GWP of chlorocarbon solvents is lower than that of most other solvents.

Appendix 2, table 4: GWP of Chlorocarbon Solvents

	GWP_{100 y} (Index, CO₂ = 1)
CFC-113	5000
HCFC-141b	620
PFC solvents	5000 – 10000
HFC-43-10mee	1300 – 1700
HFE-7100	500
Cyclic HFCs	90 – 250
HCFC-225	370
Methylene chloride	App. 9
Perchloroethylene	App. 12
Trichloroethylene	App. 5
Aliphatic solvents	5 – 50

Protection of the Operator

Several measures must be taken to ensure that the operators are fully protected from the effects of halogenated solvents. These include:

- Having equipment which is designed for low emissions or has been modified to ensure low emissions
- Ensuring that installations are correctly installed with operator protection in mind

- Ensuring that filling and emptying equipment is done according to the manufacturers' or other recommendations
- Making regular checks that the operator exposure level is respected.

New Equipment

Purchase only new equipment that minimises emissions. This does not mean that the machine must be totally enclosed. There are many lower-cost semi-enclosed machines, which are variations of open-top vapour degreasers that comply with national standards in countries with strict environmental and worker safety laws. With trichloroethylene, for example, emissions can be reduced to well under any risk of danger from operator exposure. These machines are designed with a very deep freeboard that is refrigerated to sub-zero temperatures. The opening is often fitted with automatic split sliding covers that are opened just sufficiently to allow a basket to be introduced or withdrawn in the required position. The workbaskets should be correctly dimensioned to avoid undue "piston" displacement of solvent vapours. This kind of machine usually requires an automatic hoist to make sure that the cleaning cycle is optimised. Alternatively, some form of conveyor system may be used. With such machines, OELs of between 2 and 10 ppm are usual, well under any danger level.

Retrofitted Equipment

Existing vapour-phase degreasers can often be retrofitted to reduce the workplace exposure to acceptable levels, at a lower cost than would be necessary for new equipment. Notwithstanding, retrofitting is not recommended for equipment which is already 10 years old or more. The emissions from ordinary equipment more than ten years old are dangerous for workers and the high rate of solvent use is expensive for companies. There are two major ways of achieving these aims:

- Modifying the machine to reduce emissions
- Enclosing the machine in some form of partition to prevent escaping vapours from entering the workplace.

It is sometimes necessary, especially with older equipment, to use both methods.

Modification of Machines

In general, the most successful ways of modifying the equipment are similar to those mentioned for new machines, i.e., add an extra freeboard, which is refrigerated to a low temperature; add an automatic hoist; add split sliding covers etc. In addition, it may be necessary to modify the baskets that are used for holding the work pieces and a few other minor modifications. Similar precautions may be added to tanks used for cold cleaning. Care must be taken to reduce the risk of leaks by a regular maintenance schedule and the provision of a catch tray to ensure that solvent can be recuperated should a leak occur.

Enclosing Machines

If an emissive machine were placed in a hermetic enclosure, into which the operators never entered, they would be totally protected from any emissions. In practice, the enclosure will rarely be hermetic. The main implication is that the parts to be cleaned must be introduced into the machine through some form of door or curtain, using an automatic hoist. The vapours, being heavier than air, will tend to accumulate at the bottom, away from where the parts enter or leave the machine. Gentle extraction of the

air from the bottom of the enclosure would be advantageous, on condition that it is discharged at a point where no reflux of vapour can enter the workplace.

Retrofitted equipment can usually achieve workplace OELs in the range of 5 to 20 ppm.

Installation of Equipment

Whether the equipment be new or old, it is essential that it be installed in such a way that accidental emissions are minimised. The most important point is that the place where a machine is installed should be draught-free. It is a grave fault to install it close to a door, especially towards the exterior. The floor on which it is installed must be coated with a substance that will resist the solvent being used, so that accidental spills will not penetrate through the floor into the ground (concrete is very porous and allows solvents to penetrate rapidly). Furthermore, there should be some form of retention so that, in the event of a major accident, the total contents of the machine will be kept in such a way that they can be recovered. This may take the form of a metal catch tray or suitably coated concrete retention ramps. The same applies to all areas where drums or other containers of solvents are used or stored.

Emptying and Filling Tanks or Machines

Major emissions can occur if equipment is filled or emptied without due precautions. Solvent should always be pumped from the bottom of a container into the bottom of another container. It should never be poured, filled from a tap, or carried in an open bucket or other container. Filling a drum or tank will always displace air, laden with vapours, to outside the container. This can be entirely avoided by always ensuring that a return pipe for the displaced air connects the receiver to the source. This will not only reduce emissions, it will also reduce losses, which, over time, can amount to an economic consideration.

Drums should always be kept vertical, with the bungs up, and all the bungs must be tightly closed when solvents are not actually being transferred from or to them. If a bung-hole is fitted with a tap, this should always be removed and replaced by a tight bung when it is not actually required. Drums containing new or used solvent should always be stored in a suitably ventilated area, away from all sources of light and heat, on a well maintained, solvent-resistant floor. They should be inspected weekly. Where large quantities (i.e., more than four 200 litre, or thereabouts, drums) of halogenated solvents are stored, it may be considered worthwhile to install an electronic leak detector at floor level.

Respect of Operator Exposure Level

It is easy to check whether the exposure level is within the required limits. This is possible with both short-term and long-term methods. The short-term method consists of drawing a sample of air through a special glass tube, using a small hand pump. A coloured column will indicate the concentration of solvent in the air at that given moment. This is a very low cost method and must be practised by all users of organic solvents at regular intervals. The long-term method consists of the operator wearing a special badge for a given length of time and then sending the badge to a laboratory for analysis. This has the advantage of determining the time-weighted average that the operator has been exposed to for that period. Other variations of these methods are also available.

Note that there is doubt about whether exposure to solvents, even at small levels, has an effect on foetus development. Particular care should be taken not to expose women who are likely to conceive or who are pregnant to excessive solvent levels. It is unofficially recommended to reduce TWA exposure, in such cases, to one-third of the standard levels, as a precautionary measure, such as by reducing the hours of work where exposure can occur (rotation of tasks).

Maintenance of the equipment

As with all halogenated solvents, the highest level of danger occurs when maintaining equipment, especially large machines and storage tanks. This is not due to the toxicity of the solvents but, because of the high vapour density, residual vapours will displace air, causing suffocation. Some elementary precautions are required before performing any maintenance on such equipment. These include:

- Thoroughly ventilating the equipment before maintenance, by forced air
- If necessary, using portable compressed air breathing apparatus (note that gas masks are useless for this application)
- Always have a team of at least two persons perform the maintenance, with only one in a position of potential danger at a time and the other observing him
- If it is required to enter a tank physically, the person doing this should be roped, so that the observer can pull him out of danger if a problem arises
- If a problem does arise, the observer must, on no account, place himself in danger in order to save the person doing the maintenance (in many cases, when this has been done, both persons have been suffocated).

All equipment should be regularly inspected against the possibility of leaks. It is particularly important that all taps, gaskets, o-rings, pumps and piping be checked. If it is necessary to replace gaskets or o-rings, make sure the new ones are from a material that is resistant to the solvent being used.

A badly maintained solvent may cause chemical attack of the materials used for the construction of a cleaning machine. A regular inspection of the tanks, especially any welds, should be done. If any evidence appears of acid attack, an immediate repair by a specialist should be done; if this is not possible or if the attack is severe, replace the whole tank.

Maintenance of the Solvent

The manufacturers' instructions should be followed when maintaining a solvent. In open-top vapour-phase degreasers, it is usually sufficient to do an occasional acid acceptance test and to add additional stabilisers, if necessary. In fully closed degreasers, where little fresh solvent is added to make up the volume, a more complex titration will probably be necessary, involving additions of two stabilisers.

Never mix solvents from different manufacturers; the stabilisers may be very different and incompatible with each other.

Unstabilised, generic solvents should never be used in vapour-phase degreasers.

What to do in Case of Accidents

Do not wait for an accident to happen before reading this section!

It is essential to foresee as many cases of accidents as possible, when using any kind of chemical, including solvents. These may involve anything from a minor inconvenience to a life-threatening situation. The necessary equipment to cope with accidents should be on hand at every place where solvents are stored or used. For minor spills, an absorbent material should be available to soak up the solvent and it should then be placed in suitable sealed containers for disposal as a hazardous waste. For major spills in a contained area, the solvent should be pumped into a drum and the remainder treated as a minor spill. If there is a major spill in an unprotected zone, the first thing to do is to try to contain it into as small an area as possible and to prevent it from entering into a drain. Speed is essential to prevent undue soil pollution. It may become necessary to remove contaminated soil, concrete, or asphaltic road paving to be treated as hazardous waste. Personnel must be protected at all times when handling spills, with protective clothing and gas masks (compressed air breathing apparatus may be necessary for major spills in confined areas).

Operators should be protected at all times according to the manufacturers' recommendations and the material safety data sheets during normal use of the solvents. A first aid kit should be available at all sites where solvents are being used or stored, along with an emergency shower. It is essential that the first aid kit contain means to wash an accidental splash of solvent from the skin and, above all, from the eyes. In the case of accidental ingestion, do not induce vomiting. Call immediate medical attention. If the victim is conscious, administer activated charcoal in water. If the victim is unconscious, do not administer any liquids or solids. If an oxygen mask is available, this should be applied immediately to an unconscious victim or if he is having difficulty breathing. If the patient stops breathing, apply mouth-to-mouth resuscitation if oxygen is unavailable. In the case of cardiac arrest, which can also happen in cases of inhaling massive doses of some solvents, external heart massage (cardio-pulmonary resuscitation) may be life saving until medical help arrives. Operators should be trained in first aid techniques with regular revision.

On the principle that prevention is better than cure, all equipment should be regularly inspected against the possibility of leaks. It is particularly important that all valves, gaskets, o-rings, pumps and piping be checked. If it is necessary to replace gaskets or o-rings, make sure the new ones are from a material that is resistant to the solvent being used.

Chlorinated solvents are not normally flammable but they can cause considerable harm if they are present in a fire. Very toxic fumes can be generated. In the event of a fire in a building where solvents are being used or stored, the immediate evacuation of all personnel is strongly recommended, even if the fire starts at some distance from the solvents. Closed drums can explode. Firefighters should be warned of the presence of solvents, naming the type, and should wear chemical protection clothing and breathing apparatus.

Replacement of ODSs

Part of the planning to replace an ODS is a complete re-evaluation of the equipment and a thorough worker safety analysis. If a toxic solvent is replaced by a less toxic one, such as carbon tetrachloride by trichloroethylene, worker safety will be improved—but the level of safety may still be inadequate. More precautions should often be taken even though the new solvent is less toxic.

If a more toxic solvent replaces a low toxicity one, then particular attention must be addressed to the question of operator protection. It would usually be insufficient simply to change the solvent without adding further safety features to the machine.

As a rule, replacement of carbon tetrachloride or 1,1,1-trichloroethane would be satisfactory if trichloroethylene were used as a substitute, in cleaning applications. In a few cases, CFC-113 could also be replaced by trichloroethylene but these would be the exception rather than the rule. In all these cases, there would be a cost saving. However, CFC-113 may need to be replaced by a more sophisticated solvent, such as HCFC-225 or an HFC or HFE solvent, all of which would be more expensive than the original one. This implies very good emission control, just to keep the solvent costs reasonable. If in doubt, seek advice from a qualified consultant.

Applications

There are numerous applications for solvents: only the major ones will be evoked here, in relation to the foregoing.

Vapour-phase Degreasing and Defluxing

This is probably the easiest application to ensure low operator exposure levels, provided that correct equipment or retrofitting are specified. A typical sequence of use in an open-top vapour degreaser is as follows:

- Slow immersion of the parts to be cleaned in boiling solvent until they reach a uniform temperature equal to the boiling point: on withdrawal, there will be no vapour condensation on parts.
- Slow transfer to an immersion sump containing cold distillate, until the parts have uniformly cooled to the solvent temperature. If required, ultrasonic, or other agitation may be applied, but spraying is not recommended, as it will depress the vapour level, creating excess emissions as the level restores itself.
- Slow withdrawal into the vapour phase, above the cold distillate tank (do not displace the parts to above the boiling sump, as they may be splashed with boiling, contaminated solvent). Leave parts in the vapour phase until they have reached a uniform temperature equal to the boiling point of the solvent. No further condensation will occur at this time, not even in interstices, and the parts will be perfectly dry.
- Slow withdrawal of the parts to above the vapour level in the refrigerated freeboard zone. They should remain here for several minutes, to allow residual vapours to drain back into the machine.
- Slow withdrawal from the machine, being careful not to disturb the vapour level.
- If the machine has more than two sumps, then item 2 should be repeated for each sump.

A similar technique may be used in co-solvent vapour-phase cleaning, a more expensive variant. The parts are initially cleaned in a specific hydrocarbon solvent, usually with a high boiling point and often flammable or combustible, then vapour-phase dried, as described above, in a halogenated solvent: the vapour also acts as a non-flammable blanket for the hydrocarbon solvent, thus ensuring safety under normal operating conditions. In other words, the halogenated solvent is used to clean off the hydrocarbon solvent.

Cold Cleaning

As a rule, cold cleaning can be moderately dangerous because the solvent tanks are often relatively shallow with little vapour containment. This can be partially avoided by using deep tanks, each with a refrigerated freeboard and an overall sub-zero refrigerated freeboard, with long freeboard dwell times to ensure minimal solvent drag-out. It is with cold cleaning that partitioning the machines from the workplace is the most effective, especially if there is a specific drying zone in the machine. In some cases, it may be possible to float a 1 cm layer of water onto, say, TCE or PCE, to almost totally eliminate emissions. However, this may not be desirable in some cases, such as where the parts being cleaned are incompatible with water. The presence of water may accelerate decomposition of the solvent, especially in warm conditions, so an acid acceptance test may be necessary as routine maintenance. The water may absorb some of the acid. A test with a pH indicator paper would indicate the need to change the water when the pH drops to about 4.5–5. If using a water blanket, the tanks should either be coated with a solvent-resistant resin or made from a low-carbon stainless steel containing 2 per cent of molybdenum (e.g. 18% Ni, 8% Cr, 2% Mo).

Dry Cleaning

Modern dry-to-dry machines using perchloroethylene are the only suitable chlorinated solvent option. Machines should be programmed in such a way that it is impossible to open the door to remove the cleaned clothes until all possible solvent has been extracted. This is typically a few grams of solvent per kilogram of garments. With old machines, where drying is not optimum, it is advisable to store the extracted clothes in a separate, well-ventilated, room for 12 to 24 hours before pressing them, to eliminate residual solvent and thus better protect the pressing personnel, although it would be better to have the machine replaced by a more modern one. Alternatively, there are machines using combustible hydrocarbon solvents, which may trade off toxicity against other disadvantages.

Garment Spotting

Various solvents are used for removing stains from garments or oil spots on cloth during spinning, knitting, sewing or weaving. The latter can be reduced by taking care not to over-lubricate machines. Traditionally, 1,1,1-trichloroethane has been used for this in some factories, because it has a low toxicity. Although the quantities employed in a single factory may be small, the number of factories may be very large, with a very important aggregate consumption with 100 per cent emissions. The solvent of choice to replace this is perchloroethylene, which has the additional advantage of being less likely to promote dye running. However, PCE is more toxic than TCA and precautions should be taken to protect the operators, who typically work close to the work-pieces. Fortunately, adequate protection is easy and inexpensive. It is sufficient to place a metal tube, say about 30 mm diameter, at the back of the spotting table, closed at one end, running the whole length and to cut a slot in it, say, 8 mm wide along its length. The open end of the tube is ducted to the outside via a small ventilator, so that one can feel a small draught when placing the hand close to the slot. This will draw air from the direction of the operator's face, over the workpiece, to the exterior, with no risk of exposure. In larger factories with multiple spotting tables, they can all be connected to a single larger duct with one ventilator for all of them. Butterfly valves can be placed in the ducting, if necessary, to regulate the airflow. Operator exposure can be checked to be lower than the OEL by a low-cost portable

hand pump with a suitable tube (e.g. a Dräger Accuro with a perchloroethylene 2/a tube part no. 8101501 or an Auer or other equivalent) with the open end of the tube held close to the operator's face during actual spotting operations.

Solvent Recycling

As far as possible, solvents of all types should be recovered and recycled. It is of the greatest importance never to mix used solvents: keep each type in separate drums (as a general rule, solvent mixtures are uneconomical to recycle). These will be sent to a recycler who is capable of distilling them in fully closed equipment and blending them with the appropriate stabilisers. Such recycling facilities must be considered as "high technology" with facilities for analysis of the distillate, implying a fully equipped laboratory. Where solvents users have high emissions, it may be necessary to filter the solvent vapours from the air by either cryogenic or active carbon techniques. In the case of the latter, the recycler should be able to recover the adsorbed solvents from the carbon, usually with superheated steam, and to re-activate them for re-use. The still bottoms from recycling are usually a hazardous waste. If heavy metal content is shown to be low, they may be added to fuel used for calcining cement in an appropriate kiln fitted with scrubbers and precipitators. Note that the solvents will decompose into strong acid vapours, so that these precautions are essential. Otherwise, special precautions may be necessary in accordance with local regulations and facilities.

Aerosol Sprays

As far as possible, halogenated solvents should not be used in any form of spray technology, including aerosol cans. Operator protection is very difficult and emissions are total. Very few specific applications, such as live contact cleaning, may require it, although it would be preferable to take the contacts out-of-circuit and clean by other methods, if possible. If spray cleaning of any type is done, intensive operator training is necessary to ensure he is adequately protected and emissions are minimised.

Adhesives

Halogenated solvents are often used as solvents for adhesives. This is of doubtful advantage, but the pros and cons must be weighed up depending on the conditions in the factory using them. Most types of adhesive used in large quantities can be obtained with three systems:

- Halogenated solvents
- Hydrocarbon solvents
- Aqueous emulsions

Appendix 2, table 4: Choice between the above three systems can be summarised as follows

	Halogenated solvents	Hydrocarbon solvents	Aqueous emulsions
Flammability	None	High	None
Toxicity	High	Medium	Low
Ease of use	Good	Good	Poor
Drying	Rapid	Rapid	Slow
Substrate range	Wide (may attack some plastics)	Very wide	May not be suitable for porous substrates
Application range	Very wide	Wide	Narrow
Odour	Poor	Poor	Good
Cost	Medium	Low	Low-to-medium

It can therefore be seen that the choice of system is essentially a compromise. However, insufficient thought is often given to operator safety because of the toxicity. One document [OSHA, 1999] cites a manufacturer of aircraft seats where personnel were subjected to TWA OELs far in excess of permitted levels, due to halocarbon solvent vapour. Large users of adhesives with either halogenated or hydrocarbon solvents would be well advised to ensure adequate ventilation with solvent recovery to lower emissions, as well as to protect the personnel. Of course, in the case of hydrocarbon solvents, the equipment must be flameproofed, as well.

Conclusion

With care, non-ozone-depleting chlorocarbon solvents (TCE, PCE and MC) may be safely used at low cost, often with little or no equipment modification, as a substitute for ODSs. Emissions should be minimised in all cases. Also, and this is of prime importance, exposure levels must be monitored to ensure that they are within recommendations or legal limits. Correctly used, these solvents are safe and are very unlikely to cause any short- or long-term health problems for operators. Appropriate measures should be taken to protect the environment wherever such solvents are used or stored, especially in the event of an accidental leak.

In the case of Article 5(1) countries, it is known that over 100,000 tonnes of TCE, PCE, and MC are used annually in these nations as solvents. Concern is expressed whether this high usage is always accompanied by suitable protective measures for worker safety and the environment. Regarding both old and prospective new users, it cannot be emphasised too strongly that appropriate training in the use of these solvents, protection of the personnel and the environment (including monitoring) and first aid measures for both small and large accidents are a *sine qua non* of their employment. Such measures are mandatory and applied in nearly all non-Article 5(1) countries and it is expected that developing countries will also wish to apply them equally as part of their plans to transit to a greater industrial economy. There are many other sources of information available, for example on the Internet or from solvents manufacturers, which will help them achieve this goal, and profit from the valuable economic gains that these solvents sometimes can offer for given applications, where other methods are not suitable, for any reason.

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A.3. Appendix 3. Major Non-Article 5(1) Country Regulatory Update

United States of America (USA)

ODSs

The U.S. EPA's Global Programs Division, under Title VI of the Clean Air Act, is responsible for several programmes that protect the stratospheric ozone layer. While the number of regulations introduced in the past four years is relatively small, several rules have been promulgated from 1999 to 2002, covering ODSs and their alternatives. In addition, a single air toxics ruling for aerospace applications was published, along with a single OSHA rule related to dipping and coating operations.

In June 1999 and November 2000, the EPA published final rules that set the phase-out of methyl bromide in conformance with the Protocol phase-out schedule (25 per cent by 1999; 50 per cent by 2001; 75 per cent of the baseline by 2003 relative to the 1991 baseline and complete phase-out in 2005). In addition, under the Significant New Alternatives Policy (SNAP) program, several rules were published defining the acceptability of alternatives to ODSs. These included a ruling in May 1999, that chlorobromomethane was *unacceptable* as a substitute for metals, electronics and precision cleaning with CFC-113, 1,1,1-trichloroethane or HFC-141b or in adhesives, coatings and inks. In April 1999, HFC-43-10mee was ruled *acceptable* as a substitute for CFC-113 or 1,1,1-trichloroethane in metals cleaning. The ruling recommended a 200 ppm TWA worker exposure limit and a 400 ppm workplace exposure ceiling. In December 1999, HFE-449s1 was ruled *acceptable* as substitute for CFC-113 and 1,1,1-trichloroethane in all solvents cleaning end-uses.

In December 2000, HFE-449s1 and HFE-539sf2 were ruled *acceptable* as substitutes for HCFC-141b & HCFC-22 in metals, precision and electronics cleaning. A workplace environmental exposure level of 750 ppm was recommended. HFCPA (heptafluorocyclopentane, C₅H₃F₇) was ruled *acceptable* as substitute for HCFC-141b & HCFC-22 in metals, precision and electronics cleaning, with a 123 ppm TWA and a 500 ppm ceiling. HFC-365mfc (halogenated alkane) was ruled *acceptable* as substitute for HCFC-141b & HCFC-22 in metals, precision and electronics cleaning, with a 500 ppm acceptable exposure level. As *information*, a 50-100 ppm TWA exposure level was recommended for n-propyl bromide (nPB), and a level of 25 ppm recommended by one manufacturer was mentioned; no ruling has yet been published for this substance. Also mentioned was the NTP (National Toxicology Program) current study of reproductive, developmental, carcinogenic, and neurotoxic effects associated with exposure to nPB. Finally, in March 2002, HFE-449s1 and HFE-539sf2 were ruled *acceptable* in coatings and adhesives.

VOC

Allowable concentrations of air toxics are controlled by the National Emissions Standards for Hazardous Air Pollutants. Solvents defined as VOCs or hazardous air pollutants are sometimes used as replacements for ODSs in coating and primer formulations and a single regulation was promulgated in the four-year period. In December 2000, separate VOC levels were set for primers on large aerospace

components and fully assembled aircraft. A limit of 650 g/litre was established, compared to 350 g/litre for primers used in other applications.

HEALTH & SAFETY

The last National Institute for Occupational Safety and Health (NIOSH) guide was printed in 1997, so little further guidance on exposures to ODSs is available. A single OSHA regulation in March 1999 was promulgated for solvent use in dipping and coating operations.

The publication listed extensive rules related to protection from fire, explosion and other hazards to make OSHA Standard 1910 more understandable and useful and increase compliance options for employers. Little new in the way of actual safety procedures was covered.

EUROPE

ODSs

Regulation 2037/2000 forbidding the use of CFCs and accelerating the phase-out of HCFCs has been implemented in 2000 in the 15 EU Member States. As far as solvents are concerned, uses of HCFC-141b and HCFC-225 have been banned since 1 January 2002. There is a derogation for the precision cleaning of parts in aeronautics until 31 December 2008 but this date could be brought forward by a technical committee set up by the European Commission, without amending the regulation.

VOC

The Solvents Emissions Directive 1999/13 should have been implemented in the EU 15 Member States in 2001. However, at the end of 2002, several countries have not yet complied. It concerns over 20 industrial sectors using solvents (400,000 enterprises) and it aims at reducing VOC emissions (24 000 kt) by 65 per cent; all organic compounds having a vapour pressure of 0.01 kPa or more at 293.15 K are concerned.

For cleaning application, installations using more than 2 tonnes of solvents/year (1 tonne for solvents with high toxicity risk) are in the scope of the Directive. Limitations of emissions come from 2 constraints (see Table 1):

Maximum solvent content in mg per cubic metre in the waste gases stack stream
 Maximum percentage of fugitive emissions: total solvent losses (minus recycling) divided by total solvent consumption

Appendix 3, Table 1: Limitations of emissions come from 2 constraints

Solvent toxicity (Risk phrase #)	Maximum solvent content in waste gases stack	Limits of fugitive emissions
R45/R46/R49/R60/R61*	1) Substitution or if not possible: 2) 2 mg/Nm ³	10%(>5 T) -15%(1 to 5 T)
R40**	20 mg/Nm ³	10%(>5 T) -15%(1 to 5 T)
Others	75 mg/Nm ³	15%(>10 T)- 20%(2 to 10 T)

* Carcinogenic/mutagenic/toxic for reproduction

** Suspected carcinogens

For dry-cleaning, there is an emission limit of 20 g of solvent per kg of garments.

HEALTH & SAFETY

Chlorinated Solvents

Trichloroethylene has been reclassified on 1 July 2002 from category 3 (“possible carcinogen”) to cat. 2 (“probable carcinogen”) with an R45 risk phrase (“May cause cancer”) instead of R40 (“Possible risk of irreversible effects”). This makes its use in cleaning machines virtually very difficult for two reasons:

- It should be substituted according to the VOC Directive or, if it is not possible (real technical or economical reasons etc.), limits of emissions become very stringent (see above).
- According to most Member States’ H&S regulations and follow-up of employees’ health are stricter.

This reclassification has been severely contested¹ but the regulation does apply now. Perchloroethylene is also under scrutiny but no reclassification is envisaged as of today.

Brominated Solvents

n-Propyl bromide will very likely be reclassified in cat.2 for fertility and cat.3 for reproductive toxicity in 2003 with risk phrases R60 (“may impair fertility”) and R63 (“possible risk of harm to the unborn child”) rendering its use very difficult in cleaning machines for the same reason as trichloroethylene.

OTHERS

Climate Change Issues

Groups of experts from industry, environmental NGOs and representatives of the European Commission and Member States (ECCP) have worked on ways of limiting greenhouse gases emissions following the ratification of Kyoto Protocol by Europe.

¹ The decision was largely based on one case in a cardboard/carton factory in E. Germany before the reunification. However, this case had severe confounding factors, which render the results unreliable. TCE was widely used under uncontrolled conditions. A small number of workers, but more than would have been statistically likely, did develop cancers. The TCE was blamed for this, although there were four significant confounding factors in the study that were not taken into account:

- Other chemicals used in the same factory under bad conditions
- The probability that the TCE was stabilised with an epoxide substance (epichlorohydrin), which is a strongly suspected carcinogen and is generally no longer used as a stabiliser
- The personal habits (e.g., tobacco and alcohol) of the cancer patients.
- This was a pre-recognised cluster of cases and thus the study is "hypothesis setting" and not proof of a relationship. Large, well-conducted, cohort studies do not support the relationship.

These, combined with the small cohort, have led epidemiologists to conclude that no reliable evidence exists from this isolated case.

No specific measures concerning HFC or HFE solvents are recommended given the already low level of emissions due to niche uses and implementation of the VOC Directive.

JAPAN

ODSs

The regulatory situation regarding ozone-depleting substances has not changed in the last four years and the “Ozone layer protection by regulating specific substances Act” still controls the phase-out of OD substances in Japan.

VOC

An air pollution prevention Act exists but there is no equivalent regulation to VOC regulations in Europe and the United States. Within the chlorocarbons, in 1997, trichloroethylene and perchloroethylene were designated as hazardous air polluting substances and there is now a guideline for their emission from certain facilities or equipments such as dry cleaning machines.

Health & Safety

With regards to chlorinated solvents, commonly used as substitutes for ODSs, such as methylene chloride, trichloroethylene and perchloroethylene, regulatory definitions are as follows. Workplace environment standard (Control concentration): 100, 50, and 50 ppm, respectively. Methylene chloride is regarded as mutagenic, but the other two are not. All three are classified and regarded as possible carcinogens but their evidence is inconclusive.

OTHERS

The most recent trend in controlling chemical substances in Japan can be seen in the introduction of the so-called PRTR (Pollutant Release and Transfer Register) regulation. It was promulgated in July 1999 and came into effect in 2001. The aim of the regulation is to let industrial users voluntarily improve their control of chemical substances. This law requires those using designated chemical substances commercially, to report on their emission and transfer (for example as wastes) to the environment. The government accumulates the reported data and discloses them to the public. Those substances that are designated as reportable are those regarded to be harmful to human health, affect the lives of animals and plants, hinder their growth or are ozone depleting. They are classed into two categories and there are 354 substances in class 1 and 81 in class 2. All common chlorocarbon solvents, CFCs and HCFCs are classified as class 1 substances.

A.4. Appendix 4. Properties of Typical Solvents

Properties of typical solvents are listed in the tables. For more detail, please refer to page 107 to 122 of the 1998 STOC Assessment Report

Appendix 4, table 1: Properties of Alcohols, Ketones, Aliphatic, Aromatic, and Ester Solvents

	Methanol	Ethanol	Isopropanol	Acetone	MEK	MBK	Naptha VMP	High Flash Naptha	High Flash Naptha 140	Kerosene	C10/C11 Isoparaffin	C13 N Paraffin	C10 cycloparaffin	Toluene	Ethyl Acetate
Boiling pt (°C)	65	78.3	82.3	56.3	79.6	116.1	117-138	156-172	183-210	160-257	160-171	225-243	166-238	110.6	77.1
Melting pt (°C)	-97.7	-114	-88	-95	-124	-84	-73			-46				-95	-83
Density, (g/ml) 25 °C	0.79 (20) .786 (25)	0.785	0.785	0.793	.802	0.801	0.753	0.872	0.90	0.79	0.748	0.764	0.81	0.871	0.901
KB Value	NA	NA	NA												
Evaporation rate (butyl acetate=1)	3.5	1.8	1.7	6.6	4.78	1.62	10		~30	30	29	22	54	105	
Visc./25 °C (cp)	0.59	1.2	2.4	0.3	0.43	0.6	0.57	0.78	1.2		1.0	1.8		0.57	0.3
Spec. Heat cal/kmol	19.47	30.72	43.03	29.85	37.98	51.58					67.23	86.56		35.13	40.1
Sol. of solvent in water wt % 25 °C	100	100	100	100	27.1	1.8	tr			tr				0.053	8
Sol. of water in solvent wt % 25 °C	100	100	100	100	12.5	1.9	tr			tr					
Surf. Ten./25 °C (dynes/cm)	22.3	22.5	21.4	23.7	24.6	24				27.5				28.6	23.75
Flash Pt. TCC °C	12	14	12	-18	16	16	44	108	150	54	41	93.3	41	7.2	24
Global Warming Potential -100 yr															
OZONE-DEPLETING POTENTIAL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Atmospheric Lifetime yrs															

Sources: The Dow Chemical Company, Eastman Chemical Products Inc., Exxon Chemical Company, Chemtec solvents database

Appendix 4, table 2: Physical and Chemical Properties of Halogenated Solvents

	CFC-113	HCFC-141b	HCFC-225 ca/cb	AK-225G (HCFC-225cb)	Vertrel XF (HFC-43-10mee)	HFE-7100 (HFE-449s1)	HFE-7200 (HFE-569sf2)	Carbon tetrachloride	1,1,1-Trichloroethane	Trichloroethylene	Perchloroethylene	Methylene Chloride	n-Propyl bromide
Boiling pt (°C)	47.6	32	54	56.1	55	60	78	77	74	87	121	40	71
Melting pt (°C)	-31	-103	-131	-116	-80	-153	-135	-23	-30	-73	-22	-97	-109.9
Density, (g/ml) 25 °C	1.57	1.23	1.55	1.56	1.58	1.52	1.43	1.590	1.32	1.46	1.62	1.33	1.35(20°C)
KB Value	31	56	31	30	10	10	5		124	130	90	132	
Visc. /25 °C (cp)	0.68	0.43	0.59	0.6	0.67	0.61	0.61	0.97(20°C)	0.79	0.58	0.88(20°C)	0.425(20°C)	0.57(20°C)
Spec. Heat cal/g.25°C	0.23	0.3	0.24	0.258	0.27	0.28	0.29	0.21(20°C)	0.26	0.22	0.21	0.24	N/A
Sol. of solvent in water wt % 25 °C	0.017	0.18	0.033	0.016	140ppm	<0.002	<0.002	0.08	0.07	0.11	0.015	2.0	0.25(20°C)
Sol. of water in solvent wt % 25 °C	0.0109	0.042	0.031	0.027	490ppm.	0.0095	0.0092	0.013	0.05	0.03	0.010	0.2	N/A
Surf. Ten./25 °C (dynes/cm)	17.3	18.4	16.2	16.6	14.1	13.6	13.6	27(20°C)	25.5	29.5(20°C)	32.2(20°C)	28.1(20°C)	N/A
Flash Pt. TCC °C	None	None	None	None	None	None	None	None	None	None	None	None	None
Global Warming Potential -100 yr	6000	700	370	530	1500	390	55	1800	100	N/A	N/A	N/A	N/A
Ozone-depleting potential	0.8	0.11	0.03	0.033	No	No	No	1.1	0.1	No	No	No	*
Atmospheric Lifetime yrs	85	9.4	2.5-6.6	6.6	15	5.0	0.8	N/A	6.1	N/A	N/A	N/A	*

Note *: Currently studied by the Scientific Assessment Panel

Source: 1998 STOC Assessment Report, IPCC 2001 Technical Summary, CRC Handbook of Chemistry and Physics, The Dow Chemical Company, Great Lakes Chemical Corporation

A.5. Appendix 5. List of STOC Members

The following are the STOC Members as at 31 December 2002:

Name	Residence	Nominated by (if different)	E-mail
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A.6. Appendix 6. Glossary

Acute toxicity

A measure of the harmful effects of a substance on a living organism, due to exposure over a short period of time, usually less than one day.

Alcohol

An oxygenated hydrocarbon, usually with one -OH radical replacing a hydrogen atom. Glycols are alcohols with two -OH radicals and triols with three.

Atmospheric transport

The means whereby an ODS may be transported to the ozone layer. There are several complex mechanisms. The most common, for substances with a long residence time, is a homogenisation of the concentration by means of tropospheric mixing and diffusion. For substances with a short residence time, the most significant mechanism is by rapid uplift to the tropopause in the tropics.

Bromine

A rich brown volatile toxic liquid, the third in the series of halogens.

Bromocarbon

Any organic compound containing at least one atom of bromine, replacing an atom of hydrogen. All bromocarbons are ozone depleting but some of them have a very low ozone-depleting potential. At the time of writing, only n-propyl bromide is considered as a bromocarbon solvent. (Chlorobromomethane is also a brominated solvent but is a chlorobromocarbon.)

Carcinogenicity

The quality of a substance, which describes how it can tend to cause cancer. It is important to realise that the carcinogenicity of any substance may vary greatly between species, i.e., a substance that is carcinogenic for, say, mice, may not be for humans or even between different sub-species of mice.

Chlorine

A greenish toxic gas, the second in the series of halogen elements

Chlorocarbon

Any organic compound containing at least one atom of chlorine, replacing an atom of hydrogen. All chlorocarbons are ozone depleting but most of them have a very low ozone-depleting potential: in the context of common solvents, only carbon tetrachloride (ozone-depleting potential 1.1) and 1,1,1-trichloromethane (ozone-depleting potential 0.1) are considered as ozone depleting, the other chlorocarbon solvents having ozone-depleting potentials of less than about 0.001.

Chronic toxicity

A measure of the usually irreversible harmful effects of a substance on a living organism, due to exposure of small quantities over a long period of time, usually several years. Chronic toxicity may be determined as a result of either DNA changes, such as cancer, fetus malformation etc., or direct damage to the functionality of an organ, such as a reduction of liver or brain function due to excessive consumption of alcoholic beverages over a long period of time.

Closed cleaning machine

A fully closed cleaning machine, sometimes known as a low- or zero- emission machine, consists of a chamber into which the parts to be cleaned are introduced. After the chamber is sealed, the solvents are pumped into the chamber according to a predetermined program, often finishing with solvent vapour. At the end of the cycle, a vacuum is drawn to remove the solvent vapour, before allowing air to enter, prior to removing the parts. Some similar-looking machines are not equipped with the vapour evacuation, allowing considerable quantities of solvent vapours to escape into the workplace. These are obviously cheaper but offer no advantage over a good open-top machine and may even be worse in terms of workplace exposure levels.

Epidemiology

The science of determining incidence and distribution of diseases and of other factors relating to health. In the context of solvents, it is used to relate the statistical probability of specific health problems occurring due to prolonged exposure to their vapours. This must take into account confounding factors, such as exposure to multiple chemicals and personal health habits.

Ester

A hydrocarbon with one or more hydrogen atoms replaced with an acid radical, e.g., amyl acetate

Ether

An oxygenated hydrocarbon with an oxygen atom joining two alkyl etc. groups.

Exposure badge

A badge that an operator wears close to the face, usually for one shift. It contains active carbon that absorbs solvent vapours. After use, it is sealed and sent to a laboratory for analysis with a gas chromatography. The result will give the TWA for that particular shift. It is a passive device.

Exposure tube

A glass tube containing a reagent which changes colour when exposed to a solvent vapour, the length of colour column indicating the quantity of solvent in the atmosphere. There are two types. The first is similar to the exposure badge in use and gives a direct TWA reading after a given number of hours, thus avoiding the need of a laboratory analysis, although it may be less precise. The second is useful for spot measurements in time, such as during a specifically hazardous operation which may approach the CEL. The tube is placed in a small hand pump, which allows a specific volume of air to be drawn through the tube, the open end of which is placed close to where an operator's face may be expected to be during the operation. It is also useful for general spot checks that the process is operating normally. Note that the presence of more than one kind of solvent may give erroneous results with both tube types.

Fluorine

A yellowish toxic gas, the first in the series of halogen elements

Fluorocarbon

Any organic compound containing at least one atom of fluorine, replacing an atom of hydrogen. Fluorocarbons are not generally considered as ozone depleting but they do have a very high global warming potential.

Freeboard

That part of a cleaning machine above the level of the solvent vapour or cold liquid in the machine, designed to prevent the solvent from escaping. It is often refrigerated. As a general rule of thumb, the depth of the freeboard should be equal to the diagonal of the opening. In the case of a vapour-phase degreaser, the depth is measured from the upper lip of the machine to halfway down the condenser coils.

Halocarbon

Any organic compound containing at least one atom of a halogen, replacing an atom of hydrogen. Many halocarbons, especially those containing atoms of two or more halogens, are ozone depleting.

Halogen

Any one of five monovalent non-metallic elements with unique properties. In this context, four are potential components of solvents. Fluorine; chlorine; bromine and iodine.

Halogenated

A compound is halogenated if it contains at least one atom of any halogen.

Hydrocarbon (HC)

A compound consisting of one or more carbon atoms to which only hydrogen is linked. There are many HC solvents, including generic types such as kerosene, white spirits, Stoddart's solvent, hexane, etc. and proprietary types.

Hydrocarbon/surfactant (HCS) cleaning

Also known (incorrectly) as "semi-aqueous". A cleaning process whereby organic contaminants are removed in a low-volatility hydrocarbon solvent, which is either also a surfactant or is blended with a surfactant. The contaminated solvent is then eliminated by a water wash and rinse.

Hydrohalocarbon

A partially halogenated organic compound, i.e., with some hydrogen atoms still linked to carbon. Also hydrobromocarbon (HBC), hydrochlorocarbon (HCC) and hydrofluorocarbon (HFC). Cf. perhalocarbon

Hydrolysis

In this context, the chemical breakdown of solvents, usually in the lower troposphere, by a reaction with a free hydroxyl radical, derived from airborne humidity. This is the main breakdown mechanism for non-ozone depleting and ozone-depleting ones characterised by a short residence time.

Intertropical Convergence Zone

A tropical zone, moving with the seasons, where a considerable convective uplift occurs. The trade winds converge obliquely towards it and any emissions of ozone-depleting substances within their influence will reach the tropopause within a few days if they are not otherwise decomposed by reaction with free hydroxyl radicals.

Iodine

A non-metallic, lustrous, solid halogen, giving off toxic, intense purple, vapours if heated. A few non-ozone-depleting halocarbon solvents containing iodine have been proposed but have not been widely accepted because of toxicity and stability concerns.

Lifetime

See Residence time.

“No-clean” Process

A manufacturing process that does not require a subsequent cleaning operation

Open-top cleaning machine

A machine, usually but not exclusively a vapour phase degreaser (qv), consisting of one or more tanks whereby the parts to be cleaned are introduced vertically into the solvent or solvent vapour, through an opening in the top. Such machines require a high freeboard, preferably refrigerated, and other enhancements to reduce emissions of the solvent to an acceptable level.

Ozone-depleting

A substance is said to be ozone-depleting if, when transported to the ozone layer, it will provoke a catalytic chain reaction that will cause ozone molecules to be destroyed. Most, but not all, substances that are ozone depleting are fairly stable compounds containing one or more atoms of chlorine or bromine.

Ozone layer

This is a rather imprecise term to cover the part of the earth's atmosphere where photolytic decomposition and recombination of oxygen molecules produces ozone molecules. This occurs mainly between 12 km and 50 km, so it is partly below and above the tropopause. Most of the ozone depletion due to halogen-containing chemicals and which deranges the natural equilibrium of the ozone layer occurs between 20 km and 40 km and is therefore essentially stratospheric.

Perhalocarbon

A fully halogenated organic compound, i.e., with all the hydrogen atoms replaced by one or more types of halogen atoms. Also perbromocarbon (PBC), perchlorocarbon (PCC) and perfluorocarbon (PFC). Common solvent examples are carbon tetrachloride and perchloroethylene (where the hydrogen is replaced by chlorine) and CFC-113 where three hydrogen atoms are replaced by fluorine and three by chlorine. Cf. hydrohalocarbon.

Photolysis

In this context, the breakdown of solvents by radiation with ultra-violet light. Most photolysis of solvents occurs in the stratosphere and the upper troposphere.

Residence time

In this context, the time required for solvent vapours to decompose in the atmosphere, defined as the time for its concentration to reach $1/e$ (0.3679) of its original concentration (also known as the folded-e lifetime).

“Semi-aqueous” cleaning

See Hydrocarbon/surfactant cleaning.

Stratosphere

The atmospheric layer above the tropopause, ranging in altitude from about 8-15 km to about 80 km. The temperature rises with altitude. Most of the ozone layer is situated in the stratosphere.

Sub-chronic toxicity

A measure of the harmful effects of a substance on a living organism, due to exposure of small quantities over a period of time, counting in weeks or months. This usually involves changes of functionality within the body but may be reversible, in some cases. The irreversible effect of substances on foetus development falls into this category.

Time-weighted average (TWA)

A method of expressing exposure to solvent vapours, in this context. It usually consists of the exposure level averaged over an 8 hour working day and five-day week (40 hours). For example, if an operator is exposed to 120 ppm of a substance with an OEL of 100 ppm for 8 hours in a week, it is necessary for him not to exceed 95 ppm for the remaining 32 hours ($8 \times 5 \times 100 = 8 \times 120 + 32 \times 95$) to average the 100 ppm OEL. However, the peak should never exceed the nominal CEL.

Toxicology

The scientific study of poisons. This involves the determination of means of ingress of toxic substances into the body and the chemical and metabolic changes that happen as a result, and the means and rate of elimination.

Tropopause

The atmospheric layer between the troposphere and the stratosphere, where temperature is at a minimum. Contrary to popular belief, it is not a barrier and there is considerable interchange of air across it, by several mechanisms. Its altitude varies typically from about 8 km at the poles to about 15 km at the centre of the Intertropical Convergence Zone, but can rise much higher under certain weather conditions, such as severe thunderstorms, whose uplift is often violent.

Troposphere

The atmospheric layer between the earth's surface and the tropopause. It is characterised by a reduction of temperature with altitude. Most of the earth's weather occurs in the troposphere, causing considerable mixing of gases.

Vapour phase degreasing

A process whereby the article being cleaned, at a low temperature, is placed in a solvent vapour, allowing condensation to occur on the surface. This condensed liquid, being more or less pure, rinses off any residual contaminants. It is usually used only as the final stage of a cleaning process. All cleaning action stops once the part reaches the temperature of the vapour, when the part becomes dry because no further condensation occurs.