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Leather Unit

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION (UNIDO)
Technical Information on Industrial Processes

ENVIRONMENTAL ASPECTS
of Footwear and Leather Products Manufacture

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Abbreviations and informative notes

ABS	acrylonitrile butadiene styrene
CFC	chlorofluorocarbons
EU	EUROPEAN UNION
EVA	ethylene vinyl acetate
INESCOP	INSTITUTO ESPAÑOL DEL CALZADO Y CONEXAS, ASOCIACION DE INVESTIGACION
NAFTA	NORTH AMERICAN FREE TRADE AREA
PE	polyethylene
pcp	pentachlorophenol
ppm	parts per million
PE	polyethylene
PS	polystyrene
PU	polyurethane
PVC	poly vinyl chloride
RIM	reaction injection moulding
SATRA	SATRA FOOTWEAR TECHNOLOGY CENTRE
SBR	styrene butadiene rubber
TPU	thermoplastic polyurethane
TR	thermoplastic rubber
UK	United Kingdom
UNIDO	UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
USA	United States of America
VOC	volatile organic compound

£	English Pound (monetary unit of UK)
US$	US Dollar (monetary unit of the United States of America)

All costs have been converted to USS using the conversion rate of £ 1 = US$ 1.6169 (20/10/1997)

Executive summary

All processes and therefore all industries have an impact on the environment either good or bad and the footwear and leather goods industries are no exception. For these industries the main environmental impacts are release to the air of volatile organic compounds (VOCs) and solid waste. The pressure to reduce harm to the environment is coming from both consumers and legislation. However, legislation has the greatest impact as it is compulsory.

Most countries now have some sort of legislation concerning the environment aimed at minimizing any harmful effects of industry. However while the topics of the legislation may be similar, the severity of the law and how it is implemented and enforced varies considerably. Even within individual countries there can be local variations particularly if some areas are trying to encourage industry for economic reasons.

The dangers of VOCs were identified some years ago and sufficient concern generated to ensure legislation was developed. As a consequence the footwear and leather goods industries, along with everyone else, has already carried out considerable work in this area to reduce levels of VOCs. This has been achieved by two main routes; changing to the use of solvent-free preparations wherever possible and using abatement techniques to destroy VOCs released from the processes. In many cases it has been necessary to use a combination of these techniques.

Alternatives to solvent-based adhesives have been developed. Most of these are water-based systems although hot melt and cyanoacrylates have also been evaluated with some success. There are also alternative cleaning systems now on the market which are considered to be effective. Work is continuing on developing further solvent-free technologies, in particular in the areas of primers and finishes.

A number of abatement techniques are available although not all are suitable for use by the footwear and leather goods industries. The techniques include thermal combustion, catalytic combustion, adsorption, water scrubbing and biological control. Which treatment is most suitable depends on the type, quantity and concentration of solvents present in the exhaust stream.

While reduction techniques are being used in the developed countries, many of the developing countries, although aware of the dangers, have yet to adopt similar measures mainly due to economic constraints. However some of the techniques are simple and relatively inexpensive to set up and operate and should be suitable for use in these countries.

The footwear industry and some areas of the leather goods industry produce relatively high levels of solid waste the majority of which is from the cutting process. While the industries use a wide range of materials including leather, textiles, coated fabrics and polymers, the majority off this type of waste is leather. Leather is a natural product prone to flaws and also does not have uniform properties therefore it is to be expected that levels of waste for leather would be higher than for synthetic materials. However, there are some measures which can be taken to reduce waste to the lowest levels possible. Waste minimisation starts with the animal husbandry to ensure that flaws and defects caused by insects and wire etc are kept to a minimum. It is also important to buy as good a quality leather as is economic to purchase as the higher quality leathers have fewer flaws. Finally it is essential to ensure effective lay planning which gives the maximum possible usage of the leather. Incentive schemes for hand cutters and automated lay planning and cutting are all effective.

Introduction

The UNIDO Leather Panel has been dealing extensively with environmental protection aspects of leather processing during the past four meetings. This forum gave valuable advises based on what UNIDO focused its orientation to pollution control problems of the tanning industry and included such components to its technical assistance projects implemented in developing countries. Recommendations of these Panel meetings led to launching a large scale programme oriented to introduction of low waste and cleaner technology, effluent treatm, occupational health and safety at work in the tanning subsector in the South-East Asia which is now one of the major activities of UNIDO.

Waste disposal, air pollution, use of adhesives and certain chemicals, trade of worn shoes have become an important issue in the last 5-10 years in the leather product industry. Pollution control problems of the footwear, leather goods and other leather products industry branches need similar attention and probably worldwide cooperation today. Certain work has already been made in this area in some industrialized countries and regional cooperation has been initiated within the EUROPEAN UNION (EU).

This review was commissioned by UNIDO for presentation at the 13th Session of the *UNIDO Leather and Leather Products Industry Panel*, Bologna, November 1997.

The review is intended to cover the environmental impacts and health issues of the footwear and leather goods industries with particular reference to solid waste, air pollution and chemicals. The review covers quantification of solid wastes, technology available for reducing environmental impact and health risks and legislation.

This report should be considered a starting point rather than a definitive document as due to the imposed time constraints, it was not possible to carry out an exhaustive search for all the data required.

Chapter I

FOOTWEAR AND LEATHER GOODS MANUFACTURE

Footwear

Footwear manufacture is a very complex procedure involving a relatively large number of processes and materials. The basic shoe constructions are:

- stuck-on (cemented),
- direct moulded (injected or vulcanized),
- welted,
- veldtschoen or stitched down,
- California (force lasted),
- moccasin.

The main processes and procedure for a stuck on sole construction are illustrated in *Figure 1*. The processes are similar for the other types of footwear but with different materials and wastes in the sole attaching.

Footwear uses a wide range of materials *including:*

1. **Upper/lining:**
   a) leather;
   b) textile (cotton, polyester, nylon);
   c) coated fabric (PVC and PU).

2. **Soling:**
   a) natural rubber/polyisoprene;
   b) reaction injection moulded polyurethane (RIM PU);
   c) polyvinyl chloride (PVC) and blends;
   d) ethylene vinyl acetate (EVA) and blends;
   e) styrene butadiene rubber (SBR);
   f) leather;
   g) thermoplastic polyurethane (TPU);
   h) thermoplastic rubber (TR).

3. **Insoles:**
   a) leatherboard;
   b) cellulose board;
   c) non-woven (polyester);
   d) leather.

4. **Insocks (sock lining):**
   a) leather;
   b) coated fabrics (PU and PVC);
   c) foams (EVA, PU, polyethylene [PE],

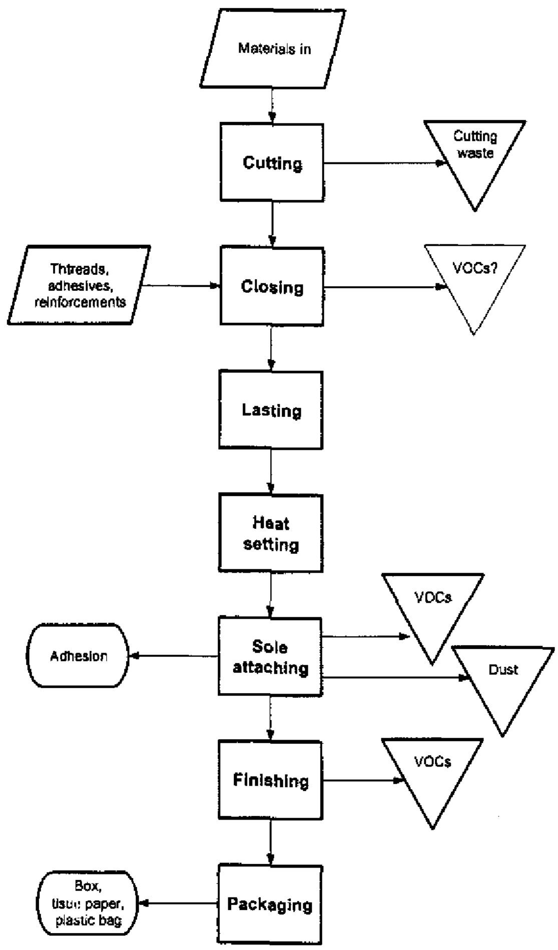

Figure 1
Main process in footwear manufacture

natural rubber latex);

d) textile (nylon)

5. Reinforcement:

a) thermoplastic sheet type (polyamide, ABS, Surlyn, EVA);
b) impregnated fabrics;
c) fabric (polyester, cotton, nylon);
d) leather;
e) fibreboard.

6. Adhesives:

a) polychloroprene;
b) polyurethane;
c) rubber based;
d) latex (natural rubber, PU, PVA).

7. Finishes:

a) lacquers (nitrocellulose, acrylic);
b) waxes and oils.

8. Cleaners:

a) petroleum spirit;
b) aqueous (mild detergent solutions).

9. Miscellaneous:

a) bottom filler (cork/resin, foam);
b) shanks (metal, wood, plastic);
c) heels (polystyrene [PS], acrylonitrile butadiene styrene [ABS]);
d) eyelets, D rings, etc. (metal, plastic);
e) laces (leather, cotton, polyester, nylon);
f) threads (cotton, polyester, nylon);
g) top pieces (TPU, vulcanized rubber, PVC);
h) fasteners (metal, plastic, fabric).

The above list, while comprehensive, is not exhaustive reinforcing the complexity of footwear.

Over the years various means have been utilized to reduce the number of process steps required of the footwear manufacturer, the most common being to supply materials pre-coated with an adhesive. While reducing production time and costs, the resulting composite nature of the material causes problems if recycling is being considered.

The main environmental effects of footwear production are solid waste, mainly from cutting, and solvents, referred to as volatile organic compounds (VOC). Solvents are also one of the main health and safety concerns in the industry along with other chemicals such as isocyanates and dust.

Leather Goods

The range of materials used in leather goods is not as wide as for footwear as it is assumed that the items will be made predominately from leather although "leather-look" alternatives are common, usually either coated leatherboard or coated fabrics.

In addition to leather, other materials used include:

- fibreboard,
- leather board,
- adhesives,
- metallic accessories,
- threads,
- fabric,
- tapes,
- finishes,
- cleaners.

The environmental effects and health and safety concerns are similar to those of the footwear industry as similar materials are used. Although cutting waste will not be as significant for small leather goods such as key fobs, watch straps etc.

Leather Products

Leather products industries include manufacture of *gloves, leather garment, saddlery, leather upholstery* and some *sports goods* (e.g. balls, protective items). The material composition of these items is even less complex than that if of leather goods, but kind of materials used is not different from those mentioned above.

Chapter II

ENVIRONMENTAL LEGISLATION

Most countries have environmental legislation but it is often very difficult to find out exactly what this legislation is in detail. The area of legislation is further complicated when countries have both national and regional legislation, e.g. USA. However one thing that is very clear is that environmental legislation is on the increase. A list of environmental legislation for some countries is given in *Table 1.*

Table 1

Environmental legislation

European Union	**Air** *Directive 84/360/EEC* - Industrial plant emissions *Regulation 594/91/EEC* - Implementing Montreal Protocol on substances which deplete the ozone layer *Directive 96/61/EEC* - Integrated Pollution Prevention and Control (IPPC) Proposed solvent Directive **Waste** *Directive 73/319/EEC* - Toxic and hazardous waste *Directive 91/156/EEC* - Waste (framework) *Directive 91/689/EEC* - Hazardous waste *Regulation 93/259/EEC* - Control of waste shipments *Directive 94/62/EEC* - Packaging and packaging waste **Hazardous substances** *Directive 76/769/EEC* - Marketing and use of certain dangerous preparations and substances *Directive 89/677/EEC* - 2-naphthylamine, 4-nitrophenyl, 4-aminodiphenyl, benzidine. *Directive 91/173/EEC* - Pentachlorophenol *Directive 91/338/EEC* - Cadmium *Directive 94/27/EEC* - Nickel **General** Proposed environmental liability legislation
Argentina	*Law No. 20, 284* - Air emissions *Law No. 23, 778* - Montreal Protocol *Law No. 24, 051* - Hazardous wastes *Law No. 23, 992* Control of Transboundary Movements of Hazardous Wastes and their Disposal
Brazil	*Federal Constitution 1988*, Article 225 *Law of National Environmental Policy* 1981 *Law 7.347* 1985 *Law 997* 1976

Finland	Air Pollution Control Act 1982 Waste Management Act 1978 Chemicals Act 1989 Nature Conservation Act 1923 Land Resources Act 1981 Planning and Building Act 1958
France	Water Resources Act 1992 *Law No.92-3* Waste Disposal Act 1992 *Law No. 92-646* *Decree No. 92-377* - Packaging waste
Mexico	General Law of Ecological Equilibrium and Environmental Protection 1988
Spain	**Air** Protection of the Atmosphere Act *Law 38 1972* *Royal Decree No. 833* 1975 **Waste** *Royal Decree 833 1988 Law 20 1986* - toxic and dangerous waste *Law 2* 1991 - reduction and management of industrial wastes *Royal Decree 319* 1991 **General** Spanish Constitution 1978, *Article 45* Spanish Constitution 1978, *Article 149* *Penal Code Section 347A* - Criminal Liability **Regional** Catalonia Protection of the Atmosphere *Act No. 22* 1983 Asturia *Decree No. 40/87* Valencia Health Service *Act No. 8/87 Section 5*
Switzerland	LPE 1985 - Protection of the environment (revised 1993?)
United Kingdom	**Air** Clean Air Act 1993 Environmental Protection (Prescribed Processes and Substances) Regulation 1991 Environmental Protection (Controls on Substances that Deplete the Ozone Layer **Waste** Special Waste Regulations 1980 Collection and Disposal of Waste Regulations 1988 Duty of Care Regulations 1991 Controlled Waste Regulations 1992 Waste Management Regulations 1996 Special Waste Regulations 1996 Landfill Tax Regulations 1996 Producer Responsibility Obligation (Packaging Waste) Regulations 1997 **Hazardous substances** Control of Injurious Substances Regulations 1993 Prescribed Substances and Processes Regulation 1991 **General** Environmental Protection Act 1990

USA	Resource Conservation and Recovery Act - Hazardous waste Comprehensive Environmental Response Compensation and Liability Act (CERCLA Superfund) Clean Air Act Toxic Substances Control Act Federal Insecticide, Fungicide and Rodenticide Act

European Union

The EUROPEAN UNION (EU) has produced a wide range of environmental legislation and looks likely to continue to do so. However the effect of EU law at national level is variable with some countries implementing legislation by the prescribed dates and some not, with the EU apparently powerless to force the issue. The situation is further complicated by the fact that Directives, which are binding, only set out the results to be achieved leaving the method of implementation to the member state. Some member states are more rigorous than others resulting in undue pressure and economic penalties for industries in some countries compared to others. Under the EU rules member states are obliged to inform the Commission of all national implementation measures. However, this is not done by all countries and again the Commission appears to be powerless to do anything. On an enquiry re the waste directive in 1994, five out of the twelve countries had not registered their national implementation measures.

EU member states can still implement national law, if it concerns the environment or human health, through **Article 100a** of the *Treaty of Rome* even if this essentially results in a barrier to trade. Germany has taken advantage of this on several occasions e.g. pentachlorophenol, azo dyes.

Despite the recent emphasis on subsidiarity, the adoption of the *Treaty on Political Union (Maastricht Treaty)* promises a growth of central power. The treaty expands the EU's power in environmental law, enhances legislative powers and for the first time empowers the EUROPEAN COURT OF JUSTICE to fine member states for failure to implement EU law.

Central and Eastern Europe

These countries have significant environmental problems compared to their western neighbours despite many of these countries having a significant body of environment law even before the opening up of Eastern Europe. These laws were fairly stringent but enforcement was negligible. Development of new laws has been a slow process in these countries with fears that stringent environmental laws will halt economic development. It can be particularly difficult to identify relevant legislation as they are not codified in single statutes or regulations but are contained in many pieces of legislation and decrees. In addition, in many of these countries the environmental law is not well defined as the general laws have few details and the necessary regulations have not been promulgated. Moreover enforcement is still not considered a top priority and any fines or penalties that do exist are not considered high enough to induce compliance.

The environmental laws in this region share some common features. Air pollution is a significant problem in these countries resulting in more stringent air pollution requirements. Countries, including Czech Republic, Poland and Hungary have established emission levels for certain pollutants. In many countries emission permits are also required. Failure to comply with regulations is generally punishable by fines.

Historically hazardous and solid wastes were disposed of without adequate protection and control and in addition it was not uncommon to import wastes from other countries for hard cash. Now many of these countries have adopted the *Basle Convention* (although sometimes this is more in theory than in practice) which restricts the import of hazardous waste from other countries. These countries are also working on waste management programmes. Under Czech law, companies which generate waste over a threshold limit must prepare a waste programme which includes descriptions of the waste generated, the disposal facilities and technical measures used to reduce waste. There is also considerable activity in the area of packaging waste following the lead of the *EU Packaging Directive*.

Argentina

Argentina has extensive environmental legislation at national, provincial and municipal levels. Some national laws have been adopted by certain provinces and others apply to activities with inter-provincial effect. This all results in a rather complex body of law.

In principle, enforcement of the environmental laws is the responsibility of the administrative authorities but action through the courts is also possible. The emphasis in recent years has been on enforcement by incentive rather than punishment and this is fairly evenly applied nationally and by the larger provinces although there are some exceptions. Further work is required to resolve some anomalies in the legislation and this is proceeding. As with most countries it is predicted that environmental law will continue to grow in significance.

Brazil

Brazil has had a well developed regulatory framework concerning the environment for some years but enforcement between and even within the different states has varied enormously. In some cases lack of enforcement is motivated purely by the need to attract industry to ensure economic development.

The duty to repair environmental damage was imposed in 1981 in the Law of *National Environmental Policy*. This imposes strict liability on anyone who pollutes the environment: no negligence need be proven only that pollution took place and who caused it. In fact, even if the polluter is proven to be acting legally, he is still subject to the strict liability if it is proven that environmental damage has occurred. Amendments to the law in 1989 allowed for criminal sanctions which included incarceration. This also provides the facility for criminal prosecution of corporations rather than just individuals.

Finland

Unlike most Nordic countries, Finland has no single all encompassing environmental law, rather environmental legislation consists of various individual acts and regulations, with each act covering only one specific area of environment. Generally in Finland there is good compliance with environmental legislation. Under Finnish law, environmental issues are divided into three categories: civil, criminal and administrative. The civil and criminal matters are generally dealt with by the courts.

France

While France has a number of environmental laws and regulations it does not have a comprehensive legal framework for environmental protection (1993 data).

France is divided into 22 regions, 101 departments and over 34,000 communes. Since 1982 many state responsibilities have been decentralized to these local authorities. However, most personnel are actually shared between state and local authorities. This has led to a complex web of procedures and obligations as the local authorities sometimes act in their own name and sometimes in the name of the state. The state still has power in some areas although the local authorities have to be consulted. The mayor of the commune also has powers in certain areas and can issue locally applicable regulations.

Mexico

Mexico has developed a body of environmental law in the framework of the *General Law of Ecological Equilibrium and Environmental Protection.* The general principles on which the laws are based for the different areas of pollution appear similar to European legislation. The laws include sanctions for non-compliance including fines and closure of a facility. The definition of liability under corporate law means that it is limited to the company directly involved and can not extend to companies or individuals who own or have an interest in the guilty party.

The enforcement of the environmental law has been spurred on by Mexico's membership of the NORTH AMERICAN FREE TRADE AREA (NAFTA). While not specifying environmental laws the NAFTA agreement requires that members refrain from lowering environmental standards to attract investment. Under the *Supplemental Agreement on Environmental Cooperation* each member has the right to establish their own environmental laws but also each member has agreed that these will be enforced.

Spain

Environmental regulation has become increasingly important in Spain largely instigated by the need to adopt EU standards. The *Spanish Constitution* contains specific provisions on avoiding environmental damage. It also identifies both central and regional government as being responsible for environmental law. The central government has exclusive responsibility for basic environmental legislation but the regions may establish additional protective regulations. There are a range of fines for breaches in legislation which can be imposed by local mayors, provincial governors and the INDUSTRY MINISTRY. In the case of very severe pollution or repeated breaches, the authorities have the right to close facilities down.

Switzerland

Switzerland is a federal state made up of a Confederation and its member states (23 cantons and 6 half cantons). The federal state is constitutionally empowered to legislate on the environment and a federal law for protection of the environment was enacted in 1983, the LPE. The LPE provides a legislative framework for the protection of the environment and sets out a number of general principles. The areas it covers include air pollution (Opair) and ground pollution (Osol). Some areas of the environment are still governed by other federal statutes. It is generally considered that, due to the federal statutes and ordinances enacted by the Confederation, the cantons have only limited authority to enact laws in this area. However, the enforcement of the federal laws and regulations is left to the cantons which in practice leads to some differences in organizational and procedural rules between cantons. The uniform enforcement of federal law is ensured through the supervision of a federal agency, the OFEFP. In addition the application of the federal regulations by the cantons is subject to judicial review by the FEDERAL TRIBUNAL, the highest court in Switzerland.

For non-compliance with environmental laws, severe administrative or criminal penalties can be imposed although criminal action can only be brought against individuals not corporate entities. In 1993 a draft revised law was submitted to the Swiss legislative body which would increase the punitive powers of the legislation by including a strict liability clause and provisions to introduce pollution taxes.

United Kingdom

There are numerous laws relating to the environment in the UK and regulation of this area is continuing to increase. Partly this is through implementation of EU law but also in some areas, such as air pollution and hazardous substances, the UK has been proactive producing stringent legislation independently. The legislation is enforced although many of the small companies in the UK do seem to fall through the net. There are inspectors whose job it is to ensure compliance but there are very few of these compared to the number of factories in the UK. Fines for non-compliance are unlimited and in some cases have exceeded £1 million. Private prosecutions may also be brought if the regulatory authorities fail to prosecute and pressure groups have been known to do so. As in other countries the authorities have the power to close an operation which is in breach of the laws to protect the environment.

Chapter III

SOLID MANUFACTURING WASTE

The majority of solid waste from footwear manufacture is from the cutting process and this is universal regardless of the type of footwear being made. Apart from this manufacturers will also have packaging waste, empty thread cones and, if on-site moulding is present, moulding waste. The latter is really only relevant to thermost moulding i.e. RIM PU, as any process waste from thermoplastic moulding can be granulated and reused.

Table 2 gives figures from various waste audits showing typical waste levels and composition. The highest single percentage is for leather. These figures do not include extraction dust, the majority of which is also leather. The quantity of dust is almost as much as for the leather from cutting. The figures are somewhat variable in *Table 2* but this must be expected as the data is obtained from different sources and it is unlikely that the same parameters were used in the four studies. It is generally accepted that leather cutting waste is usually between 20-45% depending on the quality of the leather and the efficiency of cutting, the average is considered to be 30%.

Table 2

Results of waste audits at footwear manufacturing sites

(All values in percentage of total waste)

	Factory 1	*Factory 2*	*Factory 3*	*Factory 4*
Leather	39	43	23	52
Synthetics	25	28	12	29
Paper/card	4	8	-	9
Moulding	-	11	54	-
Other	32	10	10*	10

Remarks: *Includes paper/card

**These figures are skewed by the exceptionally high moulding waste. If this is excluded the following percentages apply: Leather 51, Synthetics 27, Other 22.

It would probably be more meaningful to calculate tonne quantities and for leather these can be estimated based on the following assumptions:

- 2 square feet leather per pair,
- 30% leather wastage per pair,
- leather thickness 2 mm,
- density of leather 0.8 g/cm^3

Therefore average leather waste per pair is 89 g. *Table 3* gives quantities of leather waste based on pairage (detailed data by countries are given in *Tables A-1* through *A-7* in the *Annex*). Overall the estimated world leather pairage per annum is around 4,500 million pairs of shoes utilizing roughly 6,300 million square feet of leather resulting in 0.4 million tonnes of waste leather per annum based on 1995 figures.

Table 3

Estimated leather waste per country based on pairage in 1995

	Leather pairage	Waste leather
	million pairs	*tonnes*
Western Europe	638.1	60,795.9
Eastern Europe	259.3	23,077.7
North and Central America	279.3	24,857.0
South America	390.4	34,745.6
Australia and Oceania	16.3	1,450.7
Asia and Middle East	1,298.2	115,539.2
Africa	40.9	4,040.6
Total	**2,922.5**	**264,506.7**

In the developed countries this leather waste from the footwear industry is simply disposed of; in developing countries the waste is often utilized to make leather goods or thongs. In some cases the small pieces are sewn together to form a large sheet which is resprayed to give an even colour and then used to make leather accessories. Waste leather from other industries such as furniture is in much larger pieces and these are commonly sold on to the craft industries.

The majority of this leather waste from the footwear industry is coated leather, i.e. it has a polymeric coating or finish applied. The presence of this polymeric material causes problems in terms of recycling the leather in established processes such as leather board manufacture.

Leather Recycling

Apart from leather board manufacture, there are no commercially established routes for leather recycling. However, there has been considerable research carried out in this area and a number of techniques have been developed. These can basically be split into two types; those which destroy the leather structure totally and those which use leather fibres. The first group includes techniques such as chrome recovery and gelatin extraction while the latter includes use of the leather fibres as fillers in plastics and rubber materials. Various of the techniques are described below. None of the data reviewed indicated the economic viability of the various techniques, only the technical viability.

Chromium Recovery

Chromium can be removed from chrome tanned waste leather by either chemical or thermal means. Once recovered it can be reused to tan leather with no loss of properties. The chemical means include digestion of the leather in acid or alkali media and use of enzymes. Thermal methods include gasification, conventional incineration and plasma arc pyrolysis. From the studies carried out the thermal methods are considered to be more likely to be economically viable particularly if used with energy recovery. No commercial plants currently exist although it is reported that a plant capable of treating 2,500 tonnes of waste leather per annum is to be built in Spain at a cost of just over US$3 million. Incineration with energy and chromium recovery is suitable for any type of leather including coated leathers provided certain precautions are observed.

Gelatin Extraction

Gelatin is the product of partial destruction and denaturation of collagen which is the main component of skin. Leather contains 30-35% collagen and after chrome removal, provides an inexpensive raw material from which to manufacture industrial gelatin which has many uses.

Work has been carried out to look at the chemical modification of gelatin by grafting with acrylonitrile. The aim of this work was to produce new hydrophilic polymers which could be used as to produce biodegradable fibres with improved hydrophilic properties. The work was successful but it is known whether it is intended to commercialize the technique.

Soil Conditioner/Fertilizer

The use of ground up leather as a fibrous soil conditioner is feasible, particularly with vegetable tanned leather. Chrome tanned leather may present more of a problem due to the chrome content. However, if the leather is mixed with other material to reduce the overall concentration of the chrome then this route may be viable. Chrome III is an essential mineral for healthy plant growth, but as with any material, too much can cause adverse effects. There is also increasing interest in composting as a means of disposal for organic waste and it may be possible to add ground leather waste to increase the fibre content and the air filled porosity.

Use of Leather Waste as a Filler

Rubbers and plastics both commonly use fibrous fillers as reinforcing fillers. Work has been carried out by a number of institutes to evaluate the effectiveness of using leather fibres as fillers. In Sri Lanka leather fibres have been incorporated into rubber has shown that with increasing levels of leather fibre a rubber can be produced which on vulcanization can produce materials as hard as ebonite. This has led to the use of this system as an alternative to styrene in floor tiles and file covers. Trials have also been successfully carried out using this material as a replacement for styrene in footwear (e.g. heels). A patent has been filed on this application.

In Germany the use of ground leather waste in thermoplastic polymers has also been investigated. Moulded articles can be produced containing up to 95% by weight ground leather. It is claimed that this gives thermoplastics with a soft leather-like feel and a degree of water absorbency. This process is also the subject of a patent. The material can be processed on conventional injection moulding equipment and fairly complex and thin walled components can be manufactured.

Compression Moulding

Ground up leather and whole shoe can be compression moulded into board with the incorporation of a suitable polymeric binder. The process is very simple and does not require specialist machinery. The properties of the board can be altered by varying the process conditions producing materials ranging from felt-like to stiff boards. Further work is being undertaken to confirm the economic viability of this process and confirm the conditions required to produce reproducible materials. It is possible that this process could be set up in a footwear manufacturing facility to allow manufacturers to re-process their own waste.

Non-wovens

Non-wovens are normally manufactured from continuous filaments. However, it has been shown possible to incorporate leather fibres in the web giving a material with increased absorbency.

Paper Making

Leather fibres from uncoated leather can be used as a co-raw material in the manufacture of paper. Up to 10 % of leather fibres can be added. At this level the leather has been found to improve the properties of the paper particularly inter-fibre cohesion. Higher levels are difficult to process on simple equipment; in particular it is difficult to remove water quickly due to the hygroscopic nature of the leather. It is possible that in card manufacture higher levels of the leather could be used. The paper produced has an attractive appearance and could be niche marketed. The use of waste leather as a raw material is only economically feasible when the wood pulp price is high.

Chapter IV

DISPOSAL OF WORN FOOTWEAR

At some point every item of footwear purchased is disposed of. This may be because the footwear is old and shabby or simply that it is no longer in fashion. Theoretically all the footwear produced each tear will be disposed of at some time. Considering that almost 10,000 million pairs of shoes were produced in the World in 1995, this is potentially a large disposal problem.

From a survey carried out by INESCOP it was found that 85% of the people surveyed used a pair of shoes for at least a year, with half of these people using them for one to two years. The two main reasons given for disposal were physical state of the shoe (72%) and changes in fashion trends (25%). Shoe repair is not as common now as it used to be with 45% of the people never taking their shoes to be repaired; the remainder only took a fourth of their shoes to be repaired. The reasons given for not having shoes repaired were mainly due to economic factors, such as the repair being more expensive than the shoes, or the shoes being too old to be repaired.

More than 60% of the people surveyed threw their shoes in the rubbish, strangely 20% said that they kept their shoes but no longer used them. The remaining 20% were sent to charity shops or similar. Shoes sent to charity shops or put in collection bins are sold on, sometimes in the native country but the majority are sold on to developing countries. Only pairs in reasonable condition are worth selling on. There are not many footwear-only collection schemes - most are actually for clothing - but footwear is also put in.

A study carried out in 1995 by SATRA looked at the economics of recovery schemes for shoes in the UK. The most economic is the use of recycling points where consumers deposit their shoes and which are then collected when full. Schemes such as roadside collection are not viable for footwear unless part of a broader scheme. Prices for paired shoes are reported to be £ 200/t to £ 800/t depending on the quality of the footwear. Sorters report that in some cases single shoes can account for up to 50% of a load and these are currently landfilled. The estimated costs of bank schemes are estimated at £15 to £20 per tonne depending on the exact location of the scheme and end markets.

While the resale of used footwear to developing countries appears to be profitable for the companies in the developed world, the impact on the developing countries does not appear to have been considered either from the effect on the economics of the country or on the people themselves. If there is a fairly cheap source of footwear available then it is likely that this will suppress local industry as they will have difficulty competing. There are also the consideration of what effect wearing used footwear has on the wearer in terms of foot health.

There appears little scope currently to recycle footwear into alternative products. Two companies have been identified who claim to recycle footwear one in the UK and one in Germany but neither has been forthcoming with details of what they actually produce from the footwear. Separating the upper from the sole to aid recycling eg chrome recovery for leather uppered footwear, is not an economic option. If carried out by machine, then a fairly sophisticated piece of equipment would have to be used due to the shape of the footwear. If carried out manually, the labour costs would be very high. SATRA is currently undertaking research to try and develop simple techniques for recycling ground up shoes into alternative products.

Incineration with energy recovery is a viable recycling method for whole footwear. The ash left to be disposed of is less bulky than the original product but care must be taken as the Cr^{III} present in chrome tanned leather is likely to have been converted to Cr^{VI} which is highly toxic and carcinogenic. There has been some work undertaken to use this ash as a filler in the ceramics industry but it is not known what success was

Chapter V

VOLATILE ORGANIC COMPOUNDS

VOC's such as the organic solvents used in primers, adhesives and finishes are one of the main environmental impacts of the footwear industry. In recent years with concern over depletion of the ozone layer and air quality and increasing legislation, considerable efforts have been made to reduce the use of solvents. Where this is not possible then effort has concentrated on techniques which destroy the solvent vapours, converting them to compounds not harmful to the environment.

Most of the solvents used in footwear production are in sole bonding. This is a critical operation; a common cause of failure in footwear is poor sole bonding. The quantity of adhesive used depends on the size of the footwear but an average of 25g per pair can be assumed. Solvent-based adhesives are of low solids content on average 16% solids resulting in 21g of solvent released per pair.

Other footwear processes also use solvent-based materials. Shank attachment typically uses 4g of adhesive per shank. Cleaning of soles prior to bonding is also commonly carried out with solvents as is priming. For halogenation of a rubber sole typically 1.2g of solvent per sole is used. Heel lacquers and finishes make up the remainder of solvent used in the footwear industry.

Alternative Systems

There has been considerable work by adhesive manufacturers to develop solvent-free or low solvent products for the footwear industry mainly in the area of water-based adhesives; other alternatives include hot melt and cyanoacrylate systems.

Water-based Adhesives

There are a number of water-based adhesives now on the market which perform satisfactorily in sole bonding and can be used with existing equipment provided it is water-resistant. Most adhesives are based on either polyurethane or polychloroprene polymers. Slower drying times and poor moist ageing properties were the initial problems with water-based systems but these have been largely overcome with recent developments. Research carried out by SATRA and other footwear institutes has shown that water-based adhesives can provide adequate bond strength, are suitable for use in both large and small factories and are effective independent of climatic conditions. There is also the added advantage that there is reduced risk to the work force compared to the use of solvent-based systems.

The material cost for using water-based systems is similar to solvent-based. Actual cost of a two part water-based system is currently £ 7-8 per kilo compared £ 2.10-2.50 for a solvent-based system. However, the solids content for a water-based system is around 50% compared to around 16% for solvent-based which means the costs in use are similar. In a well controlled process it is possible to reduce costs using water-based. However, if an excess is used, the opposite applies. Water-based systems are more efficiently applied using machinery rather than by hand. It is possible to use modern application equipment with the water-based systems without any modification but for older machines a cost of £3,500 is estimated for suitable conversion. This cost is mainly for the replacement of pipework and the adhesion application head with corrosion-free stainless steel components. This cost would be expected to be largely offset by removing the need for extraction and its associated costs. Unlike solvent-based adhesives, water-based can also be spray applied which is highly efficient in terms of time and adhesive usage.

Water-based systems do require a longer drying time than solvent-based prior to bonding. However, a suitable rearrangement of the processes can ensure efficiency is maintained without the expense of additional drying facilities although some additional space for work in progress is likely to be required. Conventional adhesive drying arrangement such as forced air or ambient conditions are effective with the water-based systems.

In a suitably organized factory it would be expected to achieve the same throughput with water-based adhesives as with solvent-based.

Many companies are now using water-based systems either as a partial or total replacement for solvent-based particularly in the USA which has a head start on other countries in this field. Other developed countries are now converting to water-based in an effort to meet legislative requirements on solvent emissions. Many developing countries still currently use solvent-based adhesives.

Hot Melt Adhesives

Hot melt adhesives have been used for many years in the footwear industry for applications such as lasting. However, this type of one part non-reactive hot melt has not proved effective for sole bonding due to their inherent high viscosity and poor wetting properties on fibrous materials such as leather. Reactive hot melts, usually polyurethane-based, have been found to be successful in most situations. The cost of the hot melt adhesive is higher per kilo than for solvent-based but as hot melts are 100% solids the cost in use is likely to be similar to solvent-based adhesives. Hot melt do require specialist application equipment. Existing automatic application equipment such as bottom cementers is possible but can cost between £10,000 and £20,000 per machine. For one machine to be modified the cost would be in the order of £15,000 for the melter and £5,000 for a new application head. However, if two machines are modified, one melter could serve both meaning that the cost per machine would be in the order of £12,500. Equipment costs could again be offset by the cost saving through removing the need for extraction systems.

Currently throughput time is effected by the longer sole bonding times required by the new generation hot melts. However, this is an issue that is continuing to be worked on by the adhesive manufacturers.

Cyanoacrylates

Cyanoacrylates, better known as "Superglues", have not been used in the footwear industry although well established in other industries. These adhesives were originally developed for non-absorbent surfaces so unsuitable for materials such as leather. However, there are now versions available which are suitable for use with footwear materials, often without the need for surface pretreatment. While they are the most expensive of the adhesive materials, this would likely to be offset by the reduction in the number of processes required. The main drawback of cyanoacrylates currently is that specialist application machinery would be required for their use in footwear and this has yet to be developed.

Cleaning Systems

Solvents have traditionally been used to prepare surfaces prior to bonding and also to clean equipment. Alternatives to solvents are available one of the first to be commercialized being the citrus oil-based materials. However, there are now others on the market and it is known that these are being trialed by footwear manufacturers although details are currently limited.

Now that viable alternatives to solvent-based adhesives have been established, it is likely that further emphasis will be placed on finding alternatives to solvent-based surface preparation and cleaning systems.

Abatement Techniques

Where it is not possible to use solvent-free systems or where further reductions in solvent emissions than use of solvent-free adhesives is required then abatement techniques should be considered. It is no longer acceptable in the developed world to simply pump the solvents into the atmosphere as they are, therefore abatement techniques must destroy the solvents. There are a number of options available:

1. Thermal combustion

This requires considerable energy to heat solvent laden air to the correct combustion temperatures, typically around 750°C. If the temperature is not high enough, then unpleasant by products can be formed which may be more hazardous to the environment than the original solvent. Steps can be taken to minimize the energy required by reducing air volumes and introducing heat exchange between pollutant and exhaust streams. This technology is not considered viable for the majority of the footwear industry as the capital costs are high and relatively large volumes of solvent are required to make the process cost effective.

2. Catalytic combustion

This is essentially "flameless" burning through oxidation on a catalyst and is basically the same process as catalytic convertors on an automobile. These systems operate at lower temperatures, typically 300-350°C and convert most of the solvent vapour to carbon dioxide and water. This technique was demonstrated by SATRA as viable for the footwear industry in the late 80's but there was little interest at the time. More recently trials have been carried out at footwear factories to evaluate its feasibility on a larger scale. The footwear industry is different to other industries that currently use catalytic combustion in that the technique is usually used on warm air streams containing high concentrations of solvent. In any footwear factory the emissions are likely to be from a number of stacks which may not be close together with a relatively low concentration of solvent and at ambient temperatures. Demonstrations using equipment from a Danish company showed that catalytic combustion was feasible on-site. However, this would also be a relatively expensive technique for use by the footwear industry due to the high capital costs involved. In addition there would be the cost of reorganizing the operations within a site to ensure that emitted vapours are concentrated into a minimum volume of flowing air at a single outlet. It is considered unlikely that this type of system would be economic for small and medium sized factories. For example, the cost of a catalytic combustion unit to treat 9,000 m^3/hour would be in the region of £180,000 and such a unit would have an electrical power requirement of 27kW.

3. Adsorption

Adsorption is again an established technique in other industries such as coating where a single solvent with low water solubility is used. The usual adsorption medium is activated carbon, the solvent then being recovered by steam stripping. Footwear traditionally uses a mixture of solvents making the recovery of a useful product difficult. Disposable carbon beds are available for using on single operation but these have a very limited capacity and can therefore prove expensive. With increasing legislation and concern over disposal of hazardous waste, disposal of the contaminated carbon beds could also prove expensive. Recovery and reuse of the carbon beds would be technically feasible but it is not known whether this option is available.

4. Water scrubbing

This is not considered particularly practical for footwear where the low water solubility of some of the common solvents would reduce its effectiveness. There is also still the problem of the recovered solvent being a mixture which would have to be redistilled before reuse or re-sale. With increasing restrictions on permissible contaminants in water discharged to the sewer, it is also likely that disposal of the water could cause problems. If an additional process is required to recover all solvent from the water then this process would unlikely to be cost effective for the average footwear manufacturer.

5. Biological treatment

Biological treatment is essentially the effective operation of natural processes in compact and versatile plant where micro-organisms degrade polluting compounds into harmless and non-odorous compounds such as carbon dioxide, water nitrate and sulphate.

There are three main treatment technologies for VOC removal :

- biofilters,
- biotrickling filters,
- bioscrubbers.

Biofiltration (biofilters and biotrickling filters) uses micro-organisms (biomass) immobilised on a support media. Bioscrubbing processes rely on biomass supported in a liquid/aqueous phase. Biological treatment is essentially a two-stage process starting with transfer of the solvents from the gas to the liquid phase and/or absorption onto the bed material, followed by microbial oxidation into harmless substances.

The efficiency of the treatment is dependent on several factors including:

- pH,
- temperature,
- nutrient and essential element availability,
- salinity,
- humidity,
- contaminant concentration,
- contaminant solubility,
- absence of toxic inhibitors.

The most important factors are the concentration and solubility of the gas components (solvents). In biofilters the surface area is high and therefore low solvent solubility is acceptable as a high contact interface is provided to solubilise the solvents. The rate of the breakdown of the solvents depends on the type of micro-organism and the environmental conditions provided for them.

There are a number of different commercial equipment available varying in design and complexity but the basics are outlined below.

(i) Biofilters

This is the oldest of the biotechnology methods. The gas is forced through a filter bed of organic material containing micro-organisms immobilized as a biofilm. Materials such as peat and heather (Erica) mixtures are commonly used as supplying suitable nutrients, water retention, high surface area and interconnecting avoids to prevent the gas shortcutting through the bed. Heather is used as a bulking agent to maintain structure and prevent premature compaction of the bed. The support material is dampened periodically using a sprinkler system above the bed.

These systems can be very simple, at the most basic level the only power requirement being for a fan if the feed for the sprinklers is taken from a pressurized water line. Filter volumes of up to 3,000m^3 are common with volumetric loads of 100-200 m^3/h as usual.

(ii) Biotrickling filters

This is the intermediate between biofilters and bioscrubbers. Similar to biofilters the gas is forced through a packed bed of inert material supporting a biofilm. Liquid is continuously sprayed on the bed and recirculated. This means that the process can be monitored and controlled by monitoring of the water. As with the biofilter, absorption and biodegradation occur in the same bed. The biotrickling filters tend not to be used for removal of solvents with very poor solubility.

(iii) Bioscrubbers

Here the gas contacts sprayed water or a water curtain which absorbs off solvents into the liquid phase. Biodegradation then occurs in a subsequent bioreactor, for example an activated sludge tank. The aqueous phase containing suspended micro-organisms is continually recirculated. This maintains a moist biofilm, removes products of oxidation and supplies essential nutrients. The process can be precisely controlled by addition of nutrients and buffers and by liquid replacement to remove undesired products.

One of the major factors controlling the efficiency of this system is the solubility of the gas components, therefore these systems are less suited to removal of solvents with low solubility. Bioscrubbers are particularly suited to treatment of chlorinated solvents. While the gaseous pollutants are treated, this process does produce waste water which may need further treatment prior to disposal.

Biological treatments have been trialed successfully in the footwear industry. It is critical to obtain expert help in designing a system which exactly meets the needs of an individual factory in terms of solvent type and concentration.

Chapter VI

CHEMICALS

The footwear and leather goods industries have experienced increasing difficulties in recent years due to increased legislation on various chemicals. Some of this legislation has been by *EU Directive* and therefore concerned a number of countries. However, some is national. In some cases non-specific legislation has been used to restrict the import of goods, e.g. in Germany the consumer goods legislation which states a product must be fit for its purpose has been used to prevent the distribution of footwear with a strong naphthenic smell even though naphthalene itself is not specifically legislated against.

Cadmium

The European Directive on cadmium pigments and stabilizers was implemented in 1993. The restrictions were produced as cadmium is a heavy metal of recognized toxicity. However, the EU Directive does not constitute a ban, it simply restricts use in areas where cadmium is not considered essential. Cadmium pigments may not be used to give colour to polymers where alternatives exist (see *Table 4*). Some of these polymers are commonly used in the footwear and leather goods industries as leather finishes. The stabilizer legislation is slightly different in that it applies only to certain applications of PVC. These include apparel and clothing accessories, imitation leather and coated fabrics.

Table 4

Compendium pigment restrictions

Cadmium pigments may NOT be used to give colour in the following polymers (except in the case of safety applications)

Epoxy resins	Polypropylene
Polyurethanes	Cross linked polyetylene
Polyvinylchloride	Unsaturated polyesters
Cellulose acetate	Acrylonitrile methylmethacrylate
Cellulose acetate butyrate	Polyethylene terephthalate
Low density polyethylene (except as masterbatch)	Polybutylene terephthalate
Melamin formaldehyde	High impact polystyrene
Urea formaldehyde	Transparent/general purpose polystyrene

Nickel

The EU published a directive in 1994, commonly known as the *Nickel Directive*. Originally the Directive was only for costume jewellery but by the time of publication also included buttons, rivets, zips and buckles. The Directive applies to any articles which may come into prolonged contact with the skin and this is considered to include footwear and goods such as straps and belts. There is a total nickel content limit and also a migratory limit. The legislation is not yet in force as test methods for the migratory limits have not been developed. The earliest these methods are likely to be finished is the end of 1997. The reason for the legislation is that nickel is recognized as a potent allergen and there is an increasing percentage of the population developing a sensitivity to nickel.

Pentachlorophenol

In 1989 Germany introduced legislation banning the use of pentachlorophenol (pcp) in Germany and the import of materials and products containing more than 5 parts per million (ppm) pcp. The legislation was originally introduced on environmental grounds as Germany used to be one of the main producers of pcp. Due to the persistent nature of pcp, Germany therefore has higher than average levels of pcp present in its soil and water. However much was made of the fact that pcp is listed as a carcinogen by the green lobby in Germany although there appears to be no evidence that, at the levels used in leather, it is harmful to humans.

Other countries have followed Germany and introduced their own legislation: these include Denmark, Taiwan and Korea. The USA has had essentially a total ban on the use of pcp since 1987 when pcp was removed from the approved pesticide list for most non-wood related uses. The EU introduced EU-wide legislation in 1992 setting a limit of 1000 ppm. It is considered likely that the EU will lower this limit in the future.

Azo Dyes

Restrictions on azo dyes have been the latest legislation to effect footwear and leather goods manufacturers. The legislation was first introduced in Germany where it was no longer permitted to use azo dyes in consumer goods which, under the conditions of the specified test method, break down into twenty listed aromatic amines (see *Table 5* next page). The legislation was appealed against by a number of other European countries as a barrier to trade. However, Germany was permitted to keep the legislation under *Article 100a* of the *Treaty of Rome* as it was introduced for consumer protection. The protests at the legislation did produce some results in that there was clarification of exactly what it applied to, extensions of some of the compliance deadlines and introduction of limits, although test methods suitable for all materials covered by the legislation are still awaited.

Other countries have followed Germany's lead. The Netherlands introduced similar legislation in August 1996 although this is specific to clothing, footwear and bed linen. Turkey has had legislation since 1995 prohibiting the use of certain listed azo dyes and the same 20 aromatic amines in the production and processing of dyes, leather and textile goods and clothing. The list of twenty aromatic amines is also included in the French draft *Hazardous Chemicals Decree* which at the moment is bogged down in politics but is still expected to become law at some point. The EU are considering implementing EU wide legislation but before doing so, implemented studies looking at aspects such as the scientific basis for restriction and the likely economic impact on effected industries.

Table 5

Restricted aromatic amines

Chemical name	*CAS Number*
4-arminodiphenyl	92-67-1
Benzidine	92-87-5
2-amino-5-chlorotoluene	95-69-2
2-amino naphthalene	91-59-8
2-amino azotoluene	97-56-3
2-amino-4-nitrotoluene	99-55-8
4-chloroaniline	106-47-8
2,4-diaminoanisole	615-5-4
4,4'-diaminodiphenyl methane	101-77-9
3,3'-dichlorobenzidine	91-94-1
3,3'-dimethoxybenzidene	119-90-4
3,3'-dimethylbenzidene	119-93-7
3,3'-dimethyl-4,4'-diaminodiphenylmethane	838-88-0
2-methoxy-5-methylaninilne	120-71-8
4,4'-methylene bis(2-chloroaniline)	101-14-4
4,4'-oxydianiline	101-80-4
4,4'-thiodianiline	139-65-1
2-amino toluene	95-53-4
2,4-diamino toluene	95-80-7
2,4,5-trimethylaniline	137-17-7

Chlorinated Materials

Concern over the use of chemicals which could damage the Earth's stratospheric ozone came to a head in 1985 when the *British Antarctic Survey* team found the first real evidence of the depletion of the ozone layer. Certain chemicals were identified as having a significant effect on the rate of ozone depletion. This led to the setting up of the *Montreal Protocol* which entered into force on 1 January 1989. It was signed by over 50 countries including the EU, USA and Canada. The original aim was to control the production and use of chlorofluorocarbons (CFC) but was later extended to include other halogenated chemicals (*Copenhagen Agreement*). *Table 6* shows the current list of substances and control dates.

Footwear used to use CFC's as blowing agents in polymeric soling material to improve the thermal insulation but now use alternative materials. Of more concern is 1,1,1-trichloroethane which is still commonly used as a degreasing solvent and also used in some adhesives. Trichloroethane should now no longer be manufactured in the signatory countries and alternatives have been sought. For cleaning systems there are a number of alternatives now on the market, most of them water-based and some are based on natural materials, for example citrus oils.

In the EU the provisions of the *Montreal Protocol* and the *Copenhagen Agreement* (*Table 6*) were implemented by EU Regulation.

Table 6

Montreal Protocol Incorporating the Copenhagen Agreement

Substance	*Phase out schedule*
Chlorofluorocarbons	Phased out 1.1.96
Halons	Phased out 1.1.94
Carbon tetrachloride	Phased out 1.1.96
1,1,1-Trichloroethane	Phased out 1.1.96
Hydrochlorofluorocarbons	35% cut by 2010 65% cut by 2010 90% cut by 2015 99.5% cut by 2020 Phase out by 2030
Hydrobromofluorocarbons	Phased out 1.1.96
Methyl bromide	Freese at 1991 levels from 1.1.95 25% cut (on 1991 levels) by 1.1.98

Priority Candidate List

In 1982 after an extensive screening procedure, the EU selected a list of 129 substances for priority action from which blacklist substances could be selected. The list has been updated over the years and currently contains 132 substances (*Table 7* next page). A substance on the priority candidate list does not become a blacklist chemical until a daughter Directive which includes it is adopted. Blacklist substances are considered the most harmful and discharge of these substances must be reduced to such a level that pollution of the aquatic environment is prevented. The criteria for assigning blacklist status to a substance toxicity, persistence and bioaccumulation in the aquatic environment. Bioaccumulation and persistence in the sediment may also be included.

The *Priority Candidate List* has been used by some retailers as a criteria for material acceptance. Suppliers have been asked to confirm that their materials do not contain any of the listed substances. Fortunately testing has not been insisted upon as the cost would be extremely high.

Table 7

Priority Candidate List

2	2-amino-4-chlorophenol
3	Anthracene
5	Azinphos-ethyl
6	Azinphos-methyl
8	Benzidine
9	Benzyl chloride
10	Benzylidene chloride
11	Biphenyl

14	Chlosral hydrate
16	Chloroacetic acid
17	2-chloroaniline
18	3-chl oroaniline
19	4-chloroaniline
21	1-chloro-2, 4-dinitrobenzene
22	2-chloroethanol
24	4-chloro-3-methylphenol
25	l-chloronaphthalene
26	Chloronaphthalenes (technical mixture)
27	4-chloro-2-nitroaniline
28	1-chloro-2-nitrobenzene
29	1-chloro-3-nitrobenzene
30	1-chloro-4-nitrobenzene
31	4-chloro-2-nitrotoluene
32	Chloronitrotoluenes (other than 4-chloro-2-nitrotoluene)
33	2-chlorophenol
34	3-chlorophenol
35	4-chlorophenol
36	Chloroprene
37	3-chloroprene
38	2-chlorotoluene
39	3-chlorotoluene
40	4-chlorotoluene
41	2-chloro-p-toluidine
42	Chlorotoluidines (other than 2-chloro-p-toluidine)
43	Coumaphos
44	Cyanurlc chloride
45	2,4-d (including salts and esters)
47	Demetion (including demeton-o; -s; -s-methyl; -s-methyl-sulphone}
48	1,2 dibromoethane
49	Dibutyltin dichloride
50	Dibutyltin oxide
51	Dibutyltin salts (other than dibutyltin chloride and dibutyltin oxide)
52	Dichloroanilines
53	1,2-dichlorobenzene
54	1,3-dichlorobenzene

55	1,4-dichlorobenzene
56	Dichlorobenzidines
57	Dichlorodiisopropyl ether
58	1,l-dichloroethane
60	1,1-dichloroethylene
61	1,2-dichloroethylene
62	Dichloromethane
63	Dichloronitrobenzenes
64	2,4-dichlorophenol
125	Triphenyltin acetate
126	Triphenyltin chlorlde
127	Triphenyltin hydroxide
128	Vinyl chloride
129	Xylenes (technical mixture of isomers)
131	Atrazine
132	Bentazone

Chapter VII

HEALTH AND SAFETY

Potentially hazardous substances and materials exist in most factories. These substances may be bought in as chemical products or generated during the processing of materials. Bought in substances include solvent-borne adhesives and primers. A typical example of a leather processing hazard is dust created during operations such as scouring or roughing. The hazards in both footwear and leather goods factories will be similar as many of the materials and processes are similar. Chemicals considered hazardous usually have exposure limits.

The main risk, particularly in footwear, is from solvents and solvent-containing products. *Table 8* lists the main footwear processes where solvents are commonly present and the types of solvents. 1,1,1 trichloroethane has been included as, although no more is being manufactured in the signatory countries of the MONTREAL PROTOCOL, the solvent is still available and being used.

Table 8

Solvents used in the footwear industry

Area of operation	*Type of preparation*	*Solvent commonly present*	*Potential level of risk*
Upper fitting and lining lamination	Adhesives	Acetone, Methyl Ethyl Ketone (MEK), Ethyl Acetate, Toluene, Light Petroleum Spirit	Low

Area of operation	*Type of preparation*	*Solvent commonly present*	*Potential level of risk*
Toe puff and stiffener insertion	Activators	Acetone, MEK, Toluene, Methylene Chloride	Low to medium
Upper (shoe bottom) preparation	Wipes or primers	Acetone, MEK, Tetrahydrofuran (THF), Ethyl Acetate	Medium
Upper (shoe bottom) cementing	Adhesives	Acetone, MEK, Ethyl Acetate, Toluene, Light Petroleum Spirit	Medium to **high**
Bottom filling	Bottom filler	Acetone, MEK	Low
Sole priming and cementing	Wipes, primers, adhesives	Acetone, MEK, THF, Ethyl Acetate, Methylene Chloride, Light Petroleum Spirit	**High**
Heel cleaning	Wipes or dips	Light Petroleum Spirit	Medium
Heel lacquering, sole unit spraying	Lacquer	Acetone, MEK, Ethyl Acetate, Butyl Acetate, Cellosolve, Cellosolve Acetate, Toluene	Medium to **high**
Heel covering	Adhesive dip	Acetone, MEK, Ethyl Acetate, Toluene, Light Petroleum Spirit	Medium
Upper cleaning	Cleaner	Light Petroleum Spirit, Methylated Spirits, Isopropanol	Low
Upper spraying	Lacquer	Acetone, MEK, Ethyl Acetate, Butyl Acetate, MIBK, Cellosolve, Cellosolve Acetate	Medium
Sole laying (welted)	Adhesives	Light Petroleum Spirit, MEK, Toluene	**High**
Miscellaneous preparations	Spirit stiffeners, aerosol-based release agents or lubricants, leather waterproofing agents	Acetone, MEK, Toluene, Methylated Spirits, 1.2.2 Trifluoroethane, 1.1.2 Trichlorotrifluorethane (propellant)	Generally low

Dust is also a potential risk with leather dust being listed as a suspected carcinogen. Respirable dust, i.e. that with a particle size less than 5 mm, is of particular concern in that it can be inhaled deeply into the lungs, whereas larger particles tend to be trapped in the nose and throat.

In the manufacture of rubber soling and all rubber footwear, other risks include rubber fume which are the fumes given off by rubber during vulcanization. When opening a mould, the operative can be directly exposed to this and rubber fume is listed as potentially carcinogenic. Exposure to isocyanate is a risk in reaction injection moulding of polyurethane solings and boots. Isocyanates are very active chemicals and can cause severe sensitisation which can take the form of skin problems or more seriously, asthma-like complications. The release agents used in moulding are also a potential risk both from the release agent itself and from the solvent carrier.

Protective Measures

Once hazards and risks have been identified, steps can be taken to either eliminate hazardous materials and processes or find less hazardous substitutes. The next step is then to minimize emissions into the factory environment by a suitable means.

Good working practices can do much to minimize the exposure of workers to hazardous materials. For example for solvent-based materials, avoid using open containers for hand application, where possible use safety dispensers, keep lids on containers when not in use, etc.

The main source of rubber fume for direct moulded work is from the moulded sole during its initial cooling period. It has been shown that even the simple practice of placing the footwear on high racks above the breathing zone of operatives rather than at a low level behind them, as is common practice, reduces the exposure of the operative.

Generally most factories require some sort of extraction to keep the working environment safe. Care needs to be taken in the positioning (*Figure 2*) and specification of the extraction system so that it operates effectively. Typical examples of local exhaust ventilators include adhesive application benches (*Figure 3*), drying racks (*Figure 4*) and adhesive applying machines.

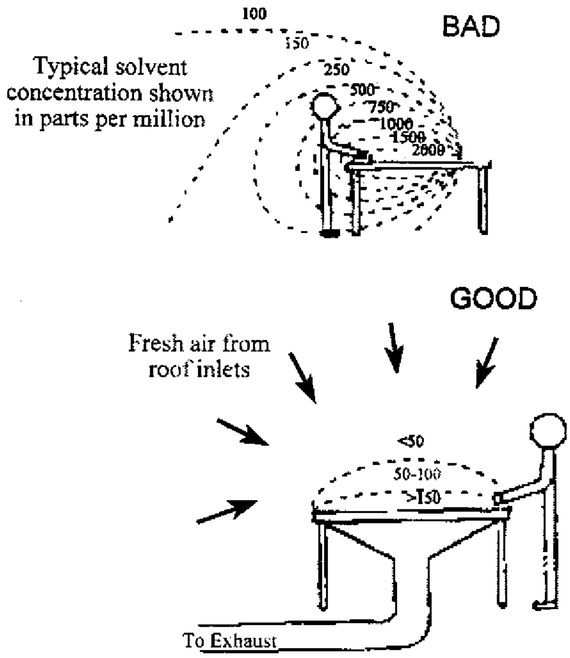

Figure 2
Ventilation of working areas

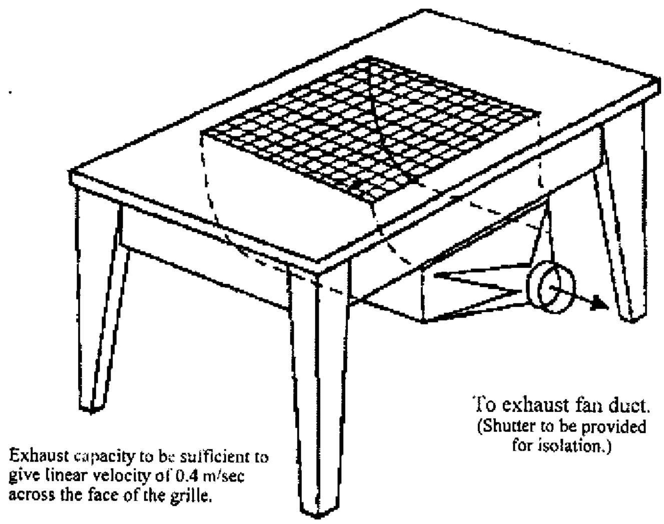

Figure 3
Work bench with grille in working surface

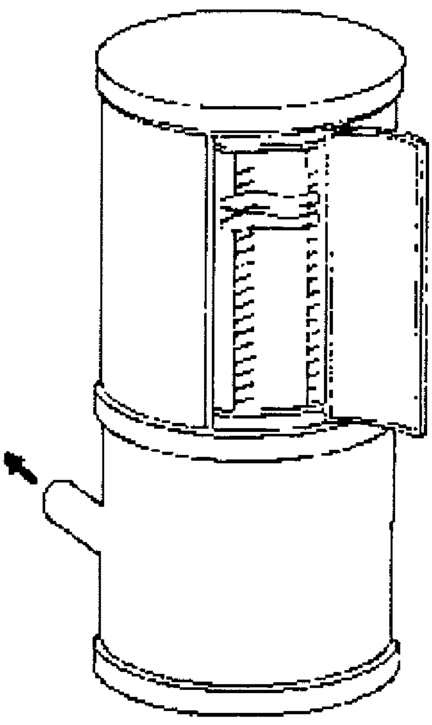

Figure 4
Extracted sole drying cabinet with rotating rack

Health and Safety Legislation

All countries have their own national legislation. In addition, for member states there is EU legislation and in USA there is both national and state legislation. However, the legislation does tend to be similar in content. Often legislation in developed countries is adopted by the developing countries. While many countries have similar legislation, the effectiveness of implementation is much more variable.

The main pieces of EU legislation which should be operative in all member states are:

- *EC Directive 89/655/EEC* - Provision and use of work equipment,
- *EC Directive 90/269/EEC* - Manual handling,
- *EC Directive 89/654/EEC* - Workplace health and safety,
- *EC Directive 89/656/EEC* - Personal protective equipment.

In the UK there are also the:

- Health and Safety at Work Act 1974,
- Control of Substances Hazardous to Health (COSHH) Regulations 1988.

In addition there are many pieces of legislation relating to specific chemicals or processes.

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Annex

Estimated leather waste per country based on pairage in 1995

Table A-1

WESTERN EUROPE

	Leather pairage (million pairs)	Waste leather (tonnes)
Austria	10.4	925.6
Belgium	1.0	89.0
Cyprus	1.5	133.5
Denmark	5.4	480.6
Eire	0.3	26.7
Finland	3.4	302.6
France	65.6	5,838.4
Germany	37.9	3,373.1
Greece	7.8	6,942.0
Italy	322.9	28,738.1
Malta	0.8	71.2
Netherlands	2.0	178.0
Norway	0.3	26.7
Portugal	41.5	3,693.5
Spain	134.8	11,997.2
Sweden	1.0	89.0
Switzerland	2.5	222.5
United Kingdom	44.0	3,916.0
Total	**683.1**	**60,795.9**

Table A-2

EASTERN EUROPE

	Leather pairage (million pairs)	Waste leather (tonnes)
Bulgaria	20.0	1,780.0
CIS	101.0	8,989.0
Czech Republic	14.9	1,326.1
Hungary	10.3	916.7
Poland	29.6	2,634.4
Romania	40.1	3,568.9
Slovakia	35.0	3,115.0
Slovenia	8.4	747.6
Total	**259.3**	**23,077.7**

Table A-3

NORTH AND CENTRAL AMERICA

	Leather pairage (million pairs)	Waste leather (tonnes)
Canada	5.1	453.9
Mexico	120.0	10,680.0
Puerto Rico	6.6	587.4
USA	147.6	13,136.4
Total	**279.3**	**24,857.7**

Table A-4

SOUTH AMERICA

	Leather pairage (million pairs)	Waste leather (tonnes)
Argentina	43.0	3,827.0
Brazil	295.9	26,335.1
Chile	11.4	1,014.6
Colombia	27.9	2,483.1
Ecuador	0.6	53.4
Venezuela	11.6	1,032.4
Total	**390.4**	**34,745.6**

Table A-5

AUSTRALIA AND OCEANIA

	Leather pairage	Waste leather
	million pairs	*tonnes*
Australia	13.1	1,165.9
New Zealand	3.2	284.8
Total	**16.3**	**1,450.7**

Table A-6

ASIA AND MIDDLE EAST

	Leather pairage	Waste leather
	million pairs	*tonnes*
Bangladesh	3.4	302.6
China	533.7	47,499.3
Hong Kong	2.6	231.4
India	198.6	17,675.4
Indonesia	52.8	4,699.2
Iran	47.3	4,209.7
Israel	5.1	453.9
Japan	23.1	2,055.9
Malaysia	20.6	1,833.4
Pakistan	75.3	6,701.1
Philippines	64.5	5,740.5
Saudi Arabia	25.6	2,278.4
Singapore	1.8	160.2
South Korea	79.0	7,031.0
Taiwan	31.2	2,776.8
Thailand	0.4	35.6
Turkey	67.9	6,043.1
Vietnam	65.3	5,811.7
Total	**1,298.2**	**115,539.2**

Table A-7

AFRICA

	Leather pairage	Waste leather
	million pairs	*tonnes*
Malawi	0.8	71.2
South Africa	25.1	2,233.9
Tunisia	9.8	872.2
Uganda	0.5	445.0
Zimbabwe	4.7	418.3
Total	**40.9**	**4,040.6**