Flexible and Integral Skin Foams Report

OORG
FOAMS SECTOR WORKING GROUP

OZONE OPERATIONS RESOURCE GROUP
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ENVIRONMENT DEPARTMENT
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Terms of Reference</td>
<td>2</td>
</tr>
<tr>
<td>Modus Operandi</td>
<td>3</td>
</tr>
<tr>
<td>Foam Density Measurement</td>
<td>4</td>
</tr>
<tr>
<td>Application Segmentation</td>
<td>4</td>
</tr>
<tr>
<td>Technology Changes with non-ODS Blowing Agents</td>
<td>6</td>
</tr>
<tr>
<td>Recommendations</td>
<td>13</td>
</tr>
<tr>
<td>Appendix I</td>
<td>13</td>
</tr>
<tr>
<td>Appendix II</td>
<td>21</td>
</tr>
</tbody>
</table>
1) INTRODUCTION

In the first half of 2000 the OORG Foams Working Group undertook a study for the Executive Committee (ExCom) of the Multilateral Fund (MLF) on the factors which affect foam density. This study, which was completed at the end of June 2000, concentrated on rigid polyurethane insulating foams. This was because the impact of technology based on alternatives to CFC 11 is greatest in these foams. Both the main alternatives, HCFC 141b and the pentane family, can cause the stable density to increase. This report detailed the market segmentation, how density should be measured, foam densities for each segment and technology developments. The foam density information included how to consider the principle of "learning" by which an enterprise could reduce the density to a "mature" level after an initial period of operation at a higher, "safe" density. There was, in addition, a market segmentation for the moulded and integral skin segments and comments on the density issues for these sectors. Finally, there were conclusions on how the data generated should be used in MLF projects.

The ExCom considered this report in July 2000 at its 31st Meeting. The density recommendations for rigid insulating foams were accepted and Decision 31/44 stipulated that these be adopted for a period of one year. In addition, the ExCom asked that a further study be undertaken on foam densities in flexible, moulded and slabstock, foams and on integral skin foams.

This task was given to the OORG Foams Working Group for execution. The OORG Working Group considered the remit to be too narrow and that several parameters, in addition to foam density, which could impact the costs of implementing MLF projects, should also be considered. The Terms of Reference (TOR) are set out below.

2) OORG FOAMS WORKING GROUP MEMBERS

The OORG Foams Working Group is composed of experts who are considered to be at the leading edge of technology. They met at The World Bank in Washington DC on November 2nd 2000 and corresponded electronically to produce this report.
The members of the Working Group are:

Fabio Aguirre - Development Chemist, Dow Europe

Roberto Dalziel - Technical Service Manager Latin America, Huntsman Polyurethanes

Brian Fogg - Technical manager, Huntsman Polyurethanes

Bert Veenendaal - Consultant, Rappa Inc.

Viraj Vithoontien - The World Bank, Montreal Protocol Unit

The Working Group was chaired by:

Mike Jeffs - OORG Foams Expert (EHS Manager, Huntsman Polyurethanes)

3) TERMS OF REFERENCE

Following the presentation of the first report on foam density the 31st Meeting of the Executive Committee decided (Decision 31/44):
(a) to adopt the conclusions and recommendations of the technical study on foam density, as contained in Annex VIII.8 to the present report, for a period of one year for the calculation of incremental operating costs:
(b) to request the Secretariat to arrange for work on the subject to be resumed, in order to improve the conclusions. This resumed work, may include, inter alia, consideration of the costs and viability of LCD technology for small and medium-sized enterprises, within the context of existing guidelines and cost-effectiveness thresholds.

The Terms of Reference were issued by the MLF Secretariat and focused on flexible moulded and density effects. The TOR are reproduced below:

"1. Following on from the analysis presented to the Executive Committee at its 31st Meeting in document UNEP/OzL.Pro/ExCom/31/53, conduct an additional study of factors influencing, and report on, the actual changes in foam densities likely to be encountered in flexible moulded polyurethane foam when manufacture by enterprises in Article-5 countries is converted from CFC to non-CFC blowing agents.

2. In doing so, investigate and analyse:

- the relation between the performance requirements of the end-products for which the foam is being produced and the density, softness and other characteristics of the foam before and after conversion
• whether non-CFC-based technologies are available to produce flexible moulded foam in the full range of densities needed to meet pre-conversion product performance requirements, making reference to the availability and relative cost-effectiveness of technologies and equipment, including the use of carbon dioxide as an auxiliary blowing agent

• international trends in the development and optimisation of individual chemicals and formulations, and any other relevant elements of the production process, and their applicability to enterprises in Article-5 countries.

3. Draw practical conclusions and make recommendations on:

• any changes to foam densities and/or other operating parameters necessary to maintain pre-conversion performance requirements

• the impact of these changes and other concurrent modifications to the production process on the capital costs of conversion and the operating costs of the converted process

• the cost and viability of LCD and other alternative technologies for small and medium-sized enterprises, within the context of existing guidelines and cost-effectiveness thresholds.

4. Produce a supplementary report covering the above investigation, analysis and conclusions and recommendations, to be read in conjunction with the Foam Density Report 2000, by 31 January 2001.”

The Working Group considered that this TOR did not cover all the relevant parameters. It added, for clarity, that the scope should exemplify both flexible moulded and integral skin foams and also cover flexible slabstock foams as this production method is used by SMEs and they do consider the use of LCD technology. Further, the study should include changes in equipment, which may be necessary with the replacement technologies for the whole of the flexible foam and integral skin sectors.

4) MODUS OPERANDI

The Foams WG met in The World Bank on November 2nd 2000 and developed the outline of the study and report. It also listed the points, which needed additional information. The outline of the study was reported to the OORG meeting on November 3rd 2000.

The first Draft Report was circulated to WG members on 20/11/00. A second draft was prepared on the basis of comments by WG members and circulated to the WG members on 10/12/00. With further comments, the third draft was prepared and circulated on 24/12/00. This circulation included UNDP and UNIDO. The fourth draft was modified on the basis of further comments received from the WG and UNDP and circulated to the WG, UNDP and UNIDO for final comments. This version was prepared on 20/01/01 with final comments from the WG and UNDP and is submitted to the MLF Secretariat.
5) FOAM DENSITY MEASUREMENT

The measurement of density should follow the standard stipulated in the previous report, namely ISO 845. It is important in several on the foam technologies, which are considered in the report, that the overall density is measured. The integral skin foams have, as their name implies, a comparatively thick skin of densified polyurethane elastomer.

To apply this method there is a necessity to cut a sample out of the foam with uniform parallel faces. This is not always possible in smaller articles with curved surfaces, such as steering wheels and other transportation mouldings. In such cases, the difference in mass throughput (shot weights) has to be determined as accurately as possible.

To ensure consistency, the same practical methodology should be followed to determine the densities in both the baseline case and with the alternative technology.

ISO 845 is summarised in Appendix 1.

6) APPLICATION SEGMENTATION

The application segmentation is listed below for integral skin foams, flexible moulded foams and slabstock foams in Tables 1, 2 and 3 respectively.

<table>
<thead>
<tr>
<th>TABLE 1 – INTEGRAL SKIN &amp; MICROCELLULAR ELASTOMER SEGMENTATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRANSPORTATION</td>
</tr>
<tr>
<td>Steering wheels</td>
</tr>
<tr>
<td>Armrest &amp; gear shift knobs</td>
</tr>
<tr>
<td>Exterior trim</td>
</tr>
<tr>
<td>Saddles</td>
</tr>
<tr>
<td>FURNITURE</td>
</tr>
<tr>
<td>Chair bases</td>
</tr>
<tr>
<td>Arm rests</td>
</tr>
<tr>
<td>MISCELLANEOUS</td>
</tr>
<tr>
<td>Mouldings</td>
</tr>
<tr>
<td>Wood imitation</td>
</tr>
<tr>
<td>E/E cabinets</td>
</tr>
<tr>
<td>Microcellular footwear (polyether)</td>
</tr>
</tbody>
</table>

In Table 1, exterior trim refers to external protective mouldings on vehicles. Integral skin saddles are normally used on bicycles. In furniture, integral skin can be used for both the bases (usually
fitted with castor wheels) and armrests. Under miscellaneous, “mouldings” refers to rigid decorative products for use within the home for effects on walls or on furniture. These can include corniches as a plaster replacement for wall decorations. Wood imitation refers to panels used for making furniture. These rigid mouldings have comparatively thin skins with a wood effect finish. E/E cabinet mouldings are structural products for electrical and electronic applications. They have thick skins. However, in recent years thermoplastic products, such as polycarbonate and PPO (polyphenylene oxide), have largely replaced polyurethane in this market in markets where there are large production volumes to support the expensive moulds required for thermoplastics. For small series production, especially in developing countries, polyurethane is still used with epoxy moulds. It should be noted that all integral skin mouldings are produced with MDI as the isocyanate.

For Table 2 it is necessary to list the types of isocyanate used. M/T refers to blends of TDI and MDI. The number of ticks (✓) refers to the most commonly found type of isocyanate, the more ticks the more prevalent is that technology.

**TABLE 2 – FLEXIBLE MOULDED SEGMENTATION**

<table>
<thead>
<tr>
<th></th>
<th>TDI</th>
<th>M/T</th>
<th>MDI</th>
<th>BASE-LINE TECHNOLOGY</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FURNITURE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Institutional/Commercial</td>
<td>✓</td>
<td>✓✓</td>
<td>✓✓</td>
<td>ODS</td>
</tr>
<tr>
<td>Mattresses</td>
<td></td>
<td></td>
<td>✓✓</td>
<td>ODS</td>
</tr>
<tr>
<td><strong>TRANSPORTATION</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seat backs</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>ODS</td>
</tr>
<tr>
<td>Seat cushions</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>ODS</td>
</tr>
<tr>
<td>Arm/Head rests</td>
<td>✓</td>
<td>✓✓</td>
<td>✓✓</td>
<td>ODS</td>
</tr>
<tr>
<td>Saddles</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>ODS</td>
</tr>
<tr>
<td>Fascias (semi-rigid)</td>
<td></td>
<td></td>
<td></td>
<td>Non-ODS</td>
</tr>
<tr>
<td><strong>MISCELLANEOUS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packaging</td>
<td></td>
<td></td>
<td>✓✓</td>
<td>ODS</td>
</tr>
<tr>
<td>Toys</td>
<td>✓</td>
<td>✓</td>
<td>✓✓</td>
<td>Non-ODS</td>
</tr>
<tr>
<td>Sporting goods</td>
<td>✓</td>
<td>✓</td>
<td>✓✓</td>
<td>ODS/Non-ODS</td>
</tr>
</tbody>
</table>

The moulded technique for mattresses is a small segment of that market. Most mattresses are cut from flexible slabstock foams. Under transportation, it is necessary to consider seat back and cushions separately. The specification for the seat cushion requires higher properties and higher density than is the case for the seat back. “Saddles” refers to motor cycle saddles. Transportation fascias are semi-rigid foams, which are usually faced by a PVC cover. The “sporting goods” market is very diverse and could be based on either a CFC or non-CFC technology baseline.
TABLE 3 – FLEXIBLE SLABSTOCK SEGMENTATION

<table>
<thead>
<tr>
<th></th>
<th>CONTINUOUS</th>
<th>DISCONTINUOUS</th>
<th>ISOCYANATE</th>
<th>BASE-LINE TECHNOLOGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>FURNITURE &amp; MATTRESSES</td>
<td></td>
<td></td>
<td>TDI (MDI)</td>
<td>ODS/non ODS</td>
</tr>
<tr>
<td>TRANSPORTATION</td>
<td>✓</td>
<td></td>
<td>TDI</td>
<td>ODS</td>
</tr>
<tr>
<td>TEXTILE &amp; FOOTWEAR</td>
<td></td>
<td></td>
<td>TDI</td>
<td>ODS</td>
</tr>
<tr>
<td>CARPET UNDERLAY</td>
<td></td>
<td></td>
<td>TDI, MDI</td>
<td>ODS</td>
</tr>
<tr>
<td>PACKAGING</td>
<td>✓</td>
<td></td>
<td>TDI</td>
<td>ODS</td>
</tr>
</tbody>
</table>

In Table 3 differentiation is made in terms of the production method, continuous or discontinuous, which can be used. The discontinuous method for furniture and mattresses is, generally, only applied by SMEs. Except for carpet underlay and a minor part of the furniture and mattresses applications, the isocyanate used is TDI. Where MDI is used, it is without ODS. This is because this technology is a recent development. In addition, ODS are not used for all higher density, higher hardness foams. At low altitude the dividing line is about 23 kg/m³ and is lower at higher altitudes.

Any application, which has a non-ODP baseline technology, is not considered further in this report.

7) TECHNOLOGY CHANGES WITH NON-ODS BLOWING AGENTS

7.1 - INTEGRAL SKIN FOAMS & MICROCELLULAR ELASTOMERS

For the purposes of describing the CFC replacement technologies and the effects of their application, the three sub-segments of transportation, furniture and miscellaneous can be considered together. The currently available options are CO₂ (water), HCFC 141b, HFC 134a and hydrocarbons. Technologies based on the “liquid” HFCs (HFC 245fa and HFC 365mfc) are not considered here as these technologies are in their infancy and these blowing agents will not be commercially available until the second half of 2002.

CO₂ (water) technology is the most widely applied in these sub-sectors and is the preferred option provided that the mouldings meet the manufacturing specification. Its main drawback, and the reason that it is not universally applied, is the fact that skin quality is not as good as with CFC 11. The other options all give good quality skin. However, in-mould coating (IMC) is frequently used with CO₂ (water) to improve foam quality or can, indeed, be used with all the other technologies if coloured mouldings are required. When there are minor defects then these can be remedied by painting. HCFC 141b technology should only be applied if all other options are proven to be unsuitable. In general, it is only necessary to even consider this technology in transportation safety applications. However, there may be a transient situation where CO₂ (water), HFC or pentane technology is not yet available in a given country. In these cases, the
enterprise should contact suppliers to obtain the preferred non-ODS technologies rather than choose HCFC 141b.

HFC 134a has a boiling point of –26°C and a rather poor solubility in polyols. However, at the low loading required for these comparatively high-density foams, sufficient blowing agent can be dissolved in the polyol and the blend stability is sufficient for the purpose. Nevertheless, it can be difficult to use and higher than average reject rates can be experienced. It is frequently used with an IMC. In transportation integral skin mouldings, pentane can give a durable skin and is favoured for heavy-duty applications, such as in trucks. Hexane is applied for microcellular footwear elastomers if CO₂ (water) technology is unsuitable.

The various parameters associated with the different alternative-blowing agents will now be considered in turn:

**Dispensers** – The integral skin process requires a laminar, bubble-free pour or injection. Low-pressure dispensers are suitable for this purpose. For environmental reasons (hazardous waste) they should be fitted with water rather than solvent cleaning. There may be a need to replace an ODS solvent in these cases. There is likely to be a need for hoses, seals and valves to be retrofitted for use with the replacements. In the case of HFC 134a some frothing may occur and processors may prefer to use high-pressure dispensers, although its use has not been shown to be mandatory. High-pressure dispensers, modified for use with flammable components, are necessary for use with pentane.

**Moulds** – Very good temperature control is necessary, especially with CO₂ (water) technology because of the high exotherm. For low reject rates positive control with heating and cooling is required. This is normally based on water circulation. A second best option is to have mould heating (ovens) facilities for the start-up of production and then to rely on the foam exotherm to maintain the required temperature. However, short-pouring intervals can create over heating after a few cycles. Good temperature control is more difficult with epoxy moulds because of poor heat transfer properties. This can be improved with the addition of aluminium powder in the mould material or metallised mould surfaces.

**Blending Equipment** – Provided that the chemical supplier can deliver pre-blended formulations containing HFC 134a, a blender is not required. If this is not the case then an in-house facility is required. For hydrocarbons it is likely that a blender is required. There are some exceptions when a supplier can supply blends containing low levels of hydrocarbons. All the other technologies can be supplied with the blowing agent pre-blended.

**Learning** – In moulding operations the parameter to be measured is the reject rate – the proportion of mouldings produced, which are unsuitable for sale. Compensation under the MLF should only be considered if the learning costs exceed the funding provided for initial trials. This is only the case for CO₂ (water) and HFC 134a technologies. In the former case the learning is associated with minimising potential problems with skin quality. For HFC 134a problems can occur with phase separation of the blowing agent resulting in a coarse skin quality and surface blemishes.
The new process will most likely result in scrap rates being doubled. Scrap is the production that requires either repair or that which cannot be repaired for sale. It is essential to define the two categories of scrap as “Repairable” and “Non-Repairable” and also define the producers repair policy. Operators will need about two months to familiarise themselves with the new technology before the scrap rate declines to the best level without modification of the process such as tools and the process parameters. Attention to the process parameters will allow scrap to be reduced to a lower level than initially existed simply since the process has most likely not been studied and optimised in the base case.

**SME Issues** – The application of the hydrocarbon options poses the main challenges for SMEs. Equipment to ensure the safe working with flammable liquids is expensive but is necessary to meet national and international safety standards. The challenge is heightened in these foams where the density is comparatively high and, in consequence, little CFC 11 is used in the base-line case. For HFC 134a there is the need for blending equipment. For SMEs, the foaming operation can be difficult to control and reduce reject rates to an acceptable level. In these cases an SME may struggle with insufficient technical support.

**Density** – There are no general rules with regard to foam density. Developments in polyols and additives that took place concurrently with, or after ODS phase-out in developed countries, have resulted in a progressive decrease in density in many cases. The density change depends on the position of the base-line technology along this learning curve. For transportation and furniture mouldings, using CO₂ (water) technology, a density increase may be necessary at densities below 450 kg/m³ in those cases where an IMC or post-treatment (painting) cannot be applied to raise skin quality. CO₂ (water) technology can be used at densities as low as 250 kg/m³. At densities of 450 kg/m³ and above an increase in foam density is not required.

The ODS replacement technologies and the factors discussed above are summarised in Table 4.
TABLE 4 – SUMMARY OF INTEGRAL SKIN AND MICROCELLULAR ELASTOMER PARAMETERS

<table>
<thead>
<tr>
<th>NON-ODS TECHNOLOGY</th>
<th>DISPENSER</th>
<th>MOULDS TEMPERATURE CONTROL</th>
<th>BLENDING</th>
<th>LEARNING</th>
<th>SME ISSUES</th>
<th>OTHER ISSUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (water)</td>
<td>LP OK</td>
<td>YES</td>
<td>NO</td>
<td>YES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCFC 141b</td>
<td>LP OK</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFC 134a</td>
<td>LP OK</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
<td></td>
</tr>
<tr>
<td>HC (PENTANE &amp; HEXANE)</td>
<td>HP</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
<td>SAFETY</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EPOXY MOULDS OK FOR LOW VOLS. DENSITY</td>
</tr>
</tbody>
</table>

7.2 – FLEXIBLE MOULDED FOAMS

For the purposes of describing the CFC replacement technologies and the effects of their application, the three sub-segments of transportation, furniture and miscellaneous (packaging) can be considered together. The currently available options are CO₂ (water), HCFC 141b, HFC 134a and liquid carbon dioxide and gas carbon dioxide (LCD & GCD). The Working Group proposes, in line with policy and technical developments in developed countries, that HCFC 141b and HFC 134a are not considered for implementation under the MLF rules. They will not be considered further in this report.

CO₂ (water) is the most widely applied CFC replacement technology for flexible moulded foams. It is a universal standard and has only been more recently challenged by LCD and GCD technologies, which can extend the density/hardness envelope, in all cases, to the levels reached with CFCs. The choice of LCD and GCD technologies can thus be justified if the enterprise continues to need the extensive density/hardness envelope to maintain its commercial operations.

The various parameters associated with the two alternative-blowing agent technologies will now be considered in turn:

**Dispensers** – Low-pressure dispensers are suitable for use with CO₂ (water). However, with the exception of CO₂ (water) technology, there is likely to be a need for hoses, seals and valves to be retrofitted for use with the replacements. For environmental reasons (hazardous waste) they should be fitted with water rather than solvent cleaning for the mixing-heads. High-pressure dispensers are required with LCD and GCD technologies.

**Moulds** – Mould temperature affects the skin quality which can be an important issue in terms of the manufacture of mouldings to meet sales specifications. Epoxy moulds are inferior to metal moulds in temperature control because of the lower thermal conductivity of the epoxy resin. Nevertheless, acceptable temperature control is possible provided that they are fitted with temperature conditioned water circulation. In the case of mould ovens or infrared heaters this
type of mould is more problematical. The inclusion of aluminium powder in the mould or metal-treated surfaces is required to transfer the heat. As the problem of temperature control relates to heating as well as cooling and the foam process is exothermic, short-pouring intervals may create over-heating after a few cycles. Generalised quantification is difficult as the temperature development is related to part size, metal content in the mould and formulation. However, as CO$_2$ (water) technology has a higher exotherm, potential problems may increase and need to be addressed through water temperature control.

Foam systems based on CO$_2$ (water) technology require moulds that seal very well. Leaking molds cause decompression leading to poor surface and reject parts as discussed above.

Mould release agents are necessary with all technologies. There is a trend to move to water rather than VOC-based release agents. These are less robust and require a degree of learning to use them. In addition, adequate drying time is required due to the lower volatility of water compared with the solvent version.

**Blending Equipment** – This equipment is only required for LCD and GCD technologies.

**Learning** – As for integral skin foams, the parameter to be measured is the reject rate – the proportion of mouldings produced, which are unsuitable for sale. However, this sub-sector is less sensitive to rejects than is integral skin foam because the moulding is normally covered with a fabric and minor skin faults are less important. In almost all cases, and using the different technologies, the learning process can be accommodated within the allowance for initial trials.

**SME Issues** – The application of the LCD and GCD technology can be a challenge for SMEs. The equipment required includes a new mixing head and a high-pressure tank for CO$_2$. As listed above, a high-pressure dispenser is necessary.

**Density** – There are no general rules with regard to foam density. Developments in polyols and additives have resulted in a progressive decrease in density in many cases. The density change depends on the position of the base-line technology along this learning curve. For institutional, commercial and transportation mouldings, no change in density is required. In institutional mouldings, the use of LCD or GCD technology or a change in the isocyanate may be required to achieve the required density. The density ranges now achievable are:

- MDI 42 to 45 kg/m$^3$ (some transportation can be higher)
- M/T 30 to 35 kg/m$^3$
- TDI down to 30 kg/m$^3$

Packaging foams can be flexible or “semi-flexible” foams and densities can be as low as 12-15 kg/m$^3$. These densities can be achieved with modern CO$_2$ (water), systems. Currently, these systems may not be readily available in all markets.

The ODS replacement technologies and the factors discussed above are summarised in Table 5.
7.3 – FLEXIBLE SLABSTOCK FOAMS

For continuous block production, the main option now being applied globally is LCD technology. This has superceded methylene chloride (MC) as the CFC 11 replacement standard because of the health and safety concerns associated with MC. In Annex 2, there is a summary of occupational and consumer exposure concerns regarding methylene chloride. Reduced pressure technology has only been applied in a few developed country enterprises and is only economic where the line output is of the order of 7 ktpa of foam. There were no lines of this capacity in developing countries prior to the mid-1995 deadline. The use of low index additives (LIA) can reduce the use of other auxiliary blowing agents but can seldom completely replace them, making it a suitable technology for applications where MC is not successful. The same is the case for forced cooling, which can act as a supplementary technology for CO₂ (water) systems. Acetone technology is only used in the USA where this substance is exempted from the list of VOCs. There is a considerable safety risk involved in the use of a flammable substance in making open-celled foams.

For discontinuous block production, the replacement options are much fewer. LCD technology is not suitable and MC technology, with its health and safety issues, is a commonly used option. Variable pressure technology is also now available from several suppliers.

The various parameters associated with the alternative-blowing agent technologies will now be considered in turn:
Dispensers ("Wet End") – Low-pressure continuous equipment is available for all technologies. It should be understood that the meaning of high-pressure versus low-pressure metering for continuous equipment is different from discontinuous dispensers. In both cases, mechanical mixing is used and flushing after use is necessary. High-pressure metering is frequently limited to TDI, tin catalysts and/or water technology alone and serves mainly to achieve better nucleation and, therefore, a more controlled and uniform cell structure.

Consequently, all technologies only require retrofitting. In the case of acetone and MC, emission control and detection/alarm equipment is the most prevalent requirement. In the case of LCD or GCD, there are two options.

- Direct through replacement of the existing mixing head. Polyol, TDI and water (or tin octoate) are metered with high-pressure in this mixing head. The other components can be metered in the polyol manifold (medium-pressure) or directly (high-pressure).

- Indirect through keeping the existing mixing head and adding a LCD head. The equipment can also be used in the "conventional" mode for any foam not requiring LCD. When LCD is required, the existing mixing head is used to premix the polyol and the other compatible components, which are then boosted to the LCD mixing head and blended with TDI, water and LCD.

Whilst the use of LCD has been commercially proven in almost 100 installations, most of these were on Maxfoam units. On conventional and Vertifoam lines there is much less experience.

ExCom decision 24/58 allows funding based on the indirect technology.

Conveyor, etc ("Dry End") – This refers to the equipment after the foam dispensing section. The safety requirements for MC and acetone technologies are mentioned above. In the case of MC there must also be a scrubber system to prevent the vapour leaving the factory.

Learning – The parameter to be measured is the foam scrap rate. For LCD technology, this is over two years and the scrap rates should be reducing with the annual progression of 4%, 2% to 0 in the third year. For MC and reduced pressure technologies, the annual scrap rates are 3%, 2% and 1%. The scrap rate for discontinuous/box foams is negligible and can be accommodated within the trial process.

SME Issues – LCD technology is only applicable to enterprises, which have consumed at least 50 te of CFC 11 per annum. These are not considered as SMEs. SMEs may have challenges in complying with industrial hygiene requirements relating to MC, safety equipment related to acetone or the more complex processing requirements in variable pressure technology. Follow-up visits by an expert may be required.

Density – There are no issues with regard to foam density. In the continuous process, LCD technology gives densities down to 15 kg/m$^3$ but has not been proven for lower densities. With MC technology, in both continuous and discontinuous processes, the use of additives may be necessary.
The ODS replacement technologies and the factors discussed above are summarised in Table 6.

### TABLE 6 – SUMMARY OF FLEXIBLE SLABSTOCK PARAMETERS

<table>
<thead>
<tr>
<th>NON ODP TECHNOLOGY</th>
<th>WET</th>
<th>DRY</th>
<th>LEARNING/ SR</th>
<th>SME</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCD</td>
<td>DIRECT/INDIRECT</td>
<td>NO</td>
<td>YES, 2 YEARS SR*** 4,2,0 %</td>
<td>NOT APPLICABLE</td>
<td>MATURITY FOR CONVENTIONAL, VERTIFOAM, DENSITIES &lt;15 kg/m³</td>
</tr>
<tr>
<td>REDUCED PRESSURE (BOXFOAM)</td>
<td>NO</td>
<td>YES</td>
<td>DEPENDS ON ALTITUDE OF FACTORY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC</td>
<td>NO</td>
<td>VENTILATION, DETECTION, SCRUBBER</td>
<td>YES SR 3,2,1%</td>
<td>YES?</td>
<td>TANKS, SEALS, TOXICITY</td>
</tr>
<tr>
<td>MC/LIA</td>
<td>NO</td>
<td>VENTILATION, DETECTION, SCRUBBER</td>
<td>YES SR 3,2,1%</td>
<td>DEDICATED METERING SYSTEM, TANKS, SEALS, TOXICITY</td>
<td></td>
</tr>
<tr>
<td>WATER/FORCED COOLING</td>
<td>NO</td>
<td>YES</td>
<td>NO</td>
<td>NOT APPLICABLE</td>
<td>COOLING TABLE</td>
</tr>
<tr>
<td>ACETONE</td>
<td>YES, HP</td>
<td>YES</td>
<td>SAFETY</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8. RECOMMENDATIONS

1. The information and guidance contained in this report should be shared with all the implementing agencies.

2. Polyurethane integral skin (and microcellular elastomer), flexible moulded and flexible slabstock foam projects should be based on the definitions of market segments as defined in Tables 1, 2 and 3.

3. The CFC replacement technology options to be applied in MLF projects should follow the guidance given in Section 7 of this report.

4. The changes required to implement phase-out of CFCs in a proposed project should consider the guidelines listed in Section 7 and Tables 4, 5 and 6. Any deviations should be clearly stated, the reasons given and they should be specifically addressed in the project review process.
5. Density is in general not an issue for the sectors considered in this report. There are technologies such as LCD/GCD, IMC, etc., that can match the baseline densities but there may be a cost penalty through higher investment or operating costs.

6. Density may be an issue for (CO$_2$) water-based integral skin foams. In view of the diversity of systems and applications, recommendations from suppliers on locally available systems should be considered. The recommendations and the way they have been used in the project should be clearly mentioned.

7. Initially higher operating costs are related to higher reject rates that may occur during the phase-in period. The report specifies these for the different applications. When the return to the baseline reject rate requires less than 6 months, it is recommended to address the costs through the normal compensation for trials. For phase-in periods of longer than 6 months, it is recommended that the costs are included as incremental operating costs. Templates for MC and LCD exist and their application remains relevant.

8. The Working Group should be reconvened when it is deemed necessary so that it can update its findings.

M Jeffs 1/2001
APPENDIX I

DENSITY MEASUREMENT

There are several quite similar standards for measuring actual foam densities, such as DIN 53420, ISO 845 and ASTM D 1622. Actual foam density means that measurement is made without removing usually denser foam skins. Below is description based on ISO 845.

In principal minimum 100 mm x 100 mm x thickness samples are weighed, volume is measured and density is expressed in kg/m$^3$. If samples are of very low density for instance less than 30 kg/m$^3$ buoyancy may be taken in account to compensate air lift.

CELLULAR PLASTICS AND RUBBERS – DETERMINATION OF APPARENT (BULK) DENSITY

1 Scope

This International Standard specifies a method for determining the apparent overall density and the apparent core density of rigid cellular plastics, and the bulk density of semi-rigid and flexible cellular plastics and rubbers.

If the material to be tested includes skins formed during moulding, the apparent overall density or the apparent core density, or both, may be determined. If the material does not have skins formed during moulding, the term overall density is not applicable.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.


ISO 1923: 1981, Cellular plastics and rubbers - Determination of linear dimensions

3 Definitions

For the purposes of this International Standard, the following definitions apply.
3.1 **apparent overall density** (of a cellular material): The mass per unit volume of a sample, including all skins formed during moulding.

3.2 **apparent core density** (of a cellular material): The mass per unit volume of a sample after all skins formed during moulding have been removed.

3.3 **bulk density** (of a cellular material): The mass per unit volume of a material measured under specified conditions and including both permeable and impermeable voids present in the material.

4 **Apparatus**

Ordinary laboratory apparatus and

4.1 Balance, capable of determining the mass of a test piece to an accuracy of 0.5%.

4.2 **Measuring instruments**, in accordance with ISO 1923.

5 **Test pieces**

5.1 **Dimensions**

Each test piece shall be of a shape such that its volume can be easily calculated. It shall be cut without deforming the original cell structure of the material.

The size of a test piece should preferably be as large as possible, commensurate with the apparatus available and with the shape of the original material. For rigid materials, the total surface area of a test piece shall be at least 100 cm$^2$. For semi-rigid and flexible materials, the volume of a test piece shall be at least 100 cm$^3$.

For rigid materials, when the apparent overall density is being determined using test pieces cut from a larger sample, the ratio of the area of skin formed during moulding to total volume shall be the same for the test pieces as for the sample.

5.2 **Number of test pieces**

A minimum of three test pieces shall be tested for flexible materials and a minimum of five shall be tested for rigid materials.
The sample may be a manufactured object whose mass and volume can be measured accurately. Its total mass and total volume may be used to determine the sample density (see 8.3).

5.3 Conditioning

5.3.1 Wait at least 72 h after manufacture before cutting from product samples the test pieces required for measurement purposes.

If required, this period may be reduced to 48 h or 16 h if experience shows that, 48 h or 16 h after manufacture, the difference in density compared with the density 72 h after manufacture is less than 10 %.

5.3.2 The test pieces shall be kept for at least 16 h at ambient conditions or in a desiccator (dry conditions) as defined below. This conditioning period may be part of the 72 h period following manufacture.

Ambient conditions in accordance with ISO 291:

\[23 \, ^\circ C \pm 2 \, ^\circ C, \, 50 \% \pm 5 \% \text{ relative humidity}\]

or

\[27 \, ^\circ C \pm 2 \, ^\circ C, \, 65 \% \pm 5 \% \text{ relative humidity}\]

Dry conditions:

\[23 \, ^\circ C \pm 2 \, ^\circ C\]
\[27 \, ^\circ C \pm 2 \, ^\circ C\]

6 Procedure

6.1 Measure the dimensions, in millimetres, of the test pieces in accordance with ISO 1923. Make a minimum of three separate measurements of each dimension. For rigid materials in board form, make at least five measurements of the central area. Calculate the mean values for each dimension and from these measurements calculate the volumes of the test pieces.

6.2. Weigh each test piece to an accuracy of 0.5 % and record its mass in grams.
7 Expression of results

7.1 The density $\rho_a$ (apparent overall density, apparent core density or bulk density) of a test piece, in kilograms per cubic metre, is given by the formula

$$m \quad x \quad 10^6$$
$$V$$

where

$m$ is the mass, in grams, of the test piece;

$V$ is the volume, in cubic millimetres, of the test piece.

Calculate the mean value of the density from the results for all test pieces and round it to the nearest 0.1 kg/m$^3$.

NOTE - With certain low-density closed-cell materials, for example those with densities less than 30 kg/m$^3$, buoyancy may be a cause of error. Allowance for this factor may be made as follows:

**If required, this period may be reduced to 48 h or 16 h if experience shows that, 48 h or 16 h after manufacture, the difference in density compared with the density 72 h after manufacture is less than 10 %**.

$$\rho_a = \frac{m + m_a}{V} \quad x \quad 10^6$$

Where

$m_a$ is the mass, in grams, of displaced air, calculated by multiplying the volume, in cubic millimetres, of the test piece by the density, in grams per cubic millimetre, of air at atmospheric temperature and pressure. The density of air at a temperature of 23 °C and a pressure of 101 325 Pa (760 mmHg) is $1,220 \times 10^{-6}$ g/mm$^3$; the density of air at 27 °C and 101 325 Pa is $1,1955 \times 10^{-6}$ g/mm$^3$.

7.2 Calculate $\Sigma$ the standard deviation (estimated) as follows and report it to two significant figures:

$$s = \sqrt{\frac{\Sigma s^2 - n(\text{ave } x)^2}{(n-1)}}$$

where

$s$ is the estimated standard deviation;
\[x\] is the value of a single measurement;
\[\text{ave} \ x\] is the arithmetic mean of the set of measurements;
\[n\] is the number of measurements made.

8 Precision

8.1 The values given in this clause were developed from data obtained using rigid materials only and with test pieces conditioned for 72 h. Their validity for other materials and conditioning periods has yet to be determined.

8.2 Inter- and intra-laboratory precision of this test method can be expected to vary for different materials. Results of a five-laboratory round-robin test programme showed that, for certain materials, measured absolute density differences can be limited to 1.7 \% (at 95 \% confidence) within a single laboratory. Measured absolute density differences between laboratories can be limited to 2.6 \% (at 95 \% confidence) for the same materials.

8.3 The density of an item measured as a whole should agree to within 4 \% with the density measured by cutting five test pieces from the whole, for a single laboratory and material.

NOTE - The above data are based upon results from a round-robin test programme between five laboratories in the USA and reported in ASTM Research Report RB: D-20-1105 of the American Society for Testing and Materials. The most variable material included in the round-robin tests showed measured absolute differences in density of 8 \% within a laboratory and 15 \% between laboratories (at 95 \% confidence).

9 Test report

The test report shall include the following information:

a) a reference to this International Standard;
b) a complete identification of the material tested;
c) the temperature and humidity at which the test pieces were conditioned;
d) the presence or absence of surface skins and if skins were removed for testing;
e) the presence of densification, striations or other defects of the test pieces;
f) the individual test results, stating details of test piece shape, test piece dimensions and the locations from which they were taken;
g) the mean value of the density (apparent overall density, apparent core density or bulk density) and the standard deviation;

h) whether any allowance was made for buoyancy and, if so, the size of the correction and details of the temperature, pressure and relative humidity of the ambient air during the test;

i) any deviation from the procedure specified in this International Standard.
APPENDIX 2

PROPERTIES, INCLUDING HEALTH AND SAFETY REGULATIONS, FOR METHYLENE CHLORIDE

Note – The WG considered it useful to list information about the properties and characteristics of methylene chloride as an appendix to this report. It considers that project developers and potential users of methylene chloride must be informed of its properties and characteristics. This appendix should be considered as an introduction and full information should be sought from potential suppliers of methylene chloride.

1. PHYSICAL/CHEMICAL PROPERTIES

Methylene chloride's combination of properties, such as a low boiling point, relative inertness, low toxicity and non-flammability have led to its use as an auxiliary blowing agent in the foam industry. Its low photochemical ozone creation potential (PCOP) and lack of ozone depletion potential (ODP) has increased its use dramatically in the recent years, making it a significant CFC-replacement in the manufacture of polyurethane foam. The U.S. EPA has recognized this by mentioning methylene chloride under the Agency's Significant New Alternatives Program (SNAP) as an acceptable alternative to ozone depleting solvents.

Methylene chloride, or dichloromethane, is a clear, colorless liquid with a penetrating ether-like odor. Typical properties can be found in the following table:

TABLE 1: PHYSICAL PROPERTIES OF METHYLENE CHLORIDE

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>84.93</td>
</tr>
<tr>
<td>Chemical structure</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>Freezing point</td>
<td>-95°C</td>
</tr>
<tr>
<td>Boiling point (760 mm Hg)</td>
<td>40°C</td>
</tr>
<tr>
<td>Hg)</td>
<td>1.32</td>
</tr>
<tr>
<td>Specific gravity (25°C)</td>
<td>11.0</td>
</tr>
<tr>
<td>Pounds per gallon (25°C)</td>
<td>1.421</td>
</tr>
<tr>
<td>Refractive index (25°C)</td>
<td>0.41 cp</td>
</tr>
<tr>
<td>Viscosity (25°C)</td>
<td>none</td>
</tr>
<tr>
<td>Flash point (closed cup)</td>
<td>15%</td>
</tr>
<tr>
<td>LEL (25°C)</td>
<td>20%</td>
</tr>
<tr>
<td>UEL (25°C)</td>
<td>615-932°C</td>
</tr>
<tr>
<td>Ignition temperature in air</td>
<td></td>
</tr>
</tbody>
</table>

Pure, dry methylene chloride is very stable and will not produce corrosion in mild or galvanized steel, copper, nickel, lead or tin. In the presence of water, however, it may undergo very slow hydrolysis to produce small quantities of hydrogen chloride, which can lead to corrosion. This process is accelerated by elevated temperatures and the presence of alkaline or metals.
Commercially available methylene chloride is normally inhibited with small quantities of stabilizers to avoid this process. Typical stabilizers are propylene oxide and cyclohexane.

Methylene chloride is considered nonflammable but under certain circumstances it may propagate a flame. In the vapor phase and under abnormal conditions (elevated temperatures, flame, sparks etc.), it may be decomposed to give off small amounts of hydrogen chloride, carbon monoxide, and phosgene.

2. ENVIRONMENTAL IMPACT

Currently, almost all of the methylene chloride used in the USA is emitted into the air (1984: 86 %). There are no natural emission sources. The atmospheric background concentrations for methylene chloride are very low (0.02-0.04 ppb), with levels in industrial areas ranging from 0.4-4 ppb. The average atmospheric lifetime is about 6 months but can be as low as 2 months in industrial areas. Because of this relatively short lifetime MC has a negligible ozone depletion potential (0.007). Also, methylene chloride does not significantly contribute to acid rain, smog (POCP: 0.9) and global warming.

Water-borne concentrations of methylene chloride will, based on the high volatility, quickly be reduced (90-95 % reduction within 0.5-1.5 hours (1)). Both aerobic and anaerobic biodegradation has been demonstrated (1,2). As a consequence, very low concentrations of MC are present in the hydrosphere, and indeed often cannot be detected.

3. HEALTH EFFECTS

DISPOSITION AND METABOLISM

The most likely routes of human exposure will be inhalation and skin contact. Methylene chloride is absorbed through the lungs and through the skin. It can, however also be absorbed through the intestines upon ingestion. It is quite rapidly excreted, mostly through the lungs, without any chemical change. The remainder is metabolized to carbon monoxide (CO), carbon dioxide (CO2) and inorganic chloride. There are two pathways for this metabolism:

- A cytochrome P450 pathway, also called "mixed function oxidase (MFO), generating CO and CO2,
- A glutathione-S-transferase (GST) pathway, generating only CO2.

The MFO route is predominant at relatively low doses; saturation occurs at around 500 ppm. Increasing the dose above the saturation level does not lead to extra metabolism by this route. The GST route seems to be used very little in the human system. In other species (e.g. the mouse) this pathway can become the major route at sufficiently higher doses.

The generation of CO in the body is of significance. It can combine with haemoglobin in the blood, forming carboxy-haemoglobin (COHb) thus reducing the oxygen carrying capacity of the blood.
ACUTE EFFECTS

MC has a relatively low acute toxicity. High exposure (> 1,000 ppm) triggers anesthetic effects and a depressant effect on the central nervous system (CNS). The CNS effect is additive with those from other CO sources, e.g. cigarette smoking.

Some reversible effects on sensory and psychomotor function have been observed from acute exposures to 300-500 ppm, but not to lower concentrations.

Little evidence is available on oral toxicity. Swallowing of small splashes is unlikely to have significant effect.

Liquid MC is a slight skin irritant, due to the removal of natural oils in the skin.

CHRONIC EFFECTS

Long term behavioral and neurological studies have shown no significant adverse effects. There is no evidence that MC causes the irreversible chronic CNS damage sometimes diagnosed as "Danish Painters Syndrome" (solvent induced encephalopathy).

The potential carcinogenicity of MC is a controversial issue. There is one study, performed for the National Toxicology Program (NTP), that suggests carcinogenic effects of high lifetime doses in mice. Other bioassays with different animals (rat, hamster) and at lower concentrations did not confirm these findings, indicating that the association between MC exposure and carcinogenicity may be unique to mice and even then concentration related. This was supported by subsequent research, concluding that important species differences exist in metabolism between the mouse on one side, and rats, hamsters, or humans on the other side. Evidence was provided that the GST pathway of metabolism is linked to the carcinogenic response observed in mice. Since humans show a very limited ability to metabolize MC via the GST pathway, the mouse is a poor surrogate for assessing human hazard.

The above mentioned research efforts led to the development of a physiologically based pharmacokinetic (PB-PK) model to evaluate the carcinogenic risk to man from exposure to MC. Application of this model on experimental animal data concludes to no significant risk for man under current hygiene standards.

The U.S. EPA has accepted the PB-PK model, and used in its draft Update to the Health Assessment Document (HAD) for methylene chloride. Also EPA's Science Advisory Board indicated approval. OSHA, however, indicated reservations, and has based its proposed revision of the occupational exposure standard for MC on the before mentioned NTP study. The industry has submitted critical comments to this proposal, and achieved reconsideration by the agency. The effected date for the new standard delayed accordingly.

EPIDEMIOLOGY
Industrial mortality studies have shown no evidence of that methylene chloride, even at relatively high concentrations (100-350 ppm, with peaks of up to 10,000 ppm) represents a carcinogenic or cardiovascular ischemic risk to humans.

4. HEALTH AND SAFETY REGULATIONS

The US Occupational Safety and Health Administration (OSHA) in January 1997 adopted a comprehensive standard for workplace exposure to methylene chloride. The standard establishes permissible exposure limits (PELs) of 25 ppm as an 8-hour time-weighted average (TWA) and 125 ppm as a short-term exposure limit (STEL). The compliance dates vary by industry sector and size of business; all companies must be in compliance by April 2000 at the latest. The standard also requires medical surveillance and contains a number of other ancillary provisions. The ACGIH threshold limit value (TLV) is 50 ppm for an 8-hour TWA exposure.

In 1987, the US Consumer Product Safety Commission (CPSC) published a Statement of Interpretation and Enforcement Policy for household products containing methylene chloride. This policy statement establishes labeling guidance for these products under the Federal Hazardous Substances Act. In addition, the use of methylene chloride in cosmetic and food products is restricted by the Food and Drug Administration (FDA).

The EU classification was established as Carc. Cat. 3/Xn;R40 in the 23rd ATP in 1997. This classification was implemented by member states by December 1998.

Following table summarizes the regulatory information:
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OSHA PEL</strong></td>
<td>8-hour TWA</td>
<td>25 ppm</td>
</tr>
<tr>
<td></td>
<td>15-minute STEL</td>
<td>125 ppm</td>
</tr>
<tr>
<td><strong>ACGIH TLV</strong></td>
<td>8 hour TWA</td>
<td>50 ppm</td>
</tr>
<tr>
<td></td>
<td>14-minute STEL</td>
<td>--</td>
</tr>
<tr>
<td><strong>IARC Classification</strong></td>
<td></td>
<td>2B (&quot;possibly carcinogenic to humans&quot;)</td>
</tr>
<tr>
<td><strong>EU Classification</strong></td>
<td></td>
<td>Carc. Cat.3/Xn;R40</td>
</tr>
<tr>
<td><strong>CERCLA Reportable Quantity (RQ)</strong></td>
<td></td>
<td>1000 pounds</td>
</tr>
<tr>
<td><strong>Maximum Contaminant Level (Drinking Water)</strong></td>
<td></td>
<td>5 micrograms/liter (5 parts per billion)</td>
</tr>
<tr>
<td><strong>CAS Number</strong></td>
<td></td>
<td>75-09-2</td>
</tr>
<tr>
<td><strong>RCRA Hazardous Waste Number</strong></td>
<td></td>
<td>U 080</td>
</tr>
<tr>
<td><strong>DOT Hazard Classification</strong></td>
<td></td>
<td>6.1 (packing group III)</td>
</tr>
<tr>
<td><strong>DOT ID Number</strong></td>
<td></td>
<td>UN1593</td>
</tr>
</tbody>
</table>