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环 境 规 划 署

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执行蒙特利尔议定书
多边基金执行委员会
第六十六次会议
2012 年 4 月 16 日至 20 日，蒙特利尔

关于附有具体报告规定的核定项目执行情况的报告

导言

1. 秘书处请双边和执行机构向第六十六次会议提交关于项目执行情况的逾期未交进度报告，各项协定和执行委员会第五十九次和第六十五次会议之间做出的相关决定中载有具体报告要求。

2. 本文件包括下列国家的报告，这些报告是在第六十五次会议八周后的截止日期后提交的，但秘书处无法对其进行审查：布基纳法索（最终淘汰管理计划核查报告）；中国（溶剂行业进度报告和核查报告）；科特迪瓦（最终淘汰管理计划核查报告）；印度尼西亚（国家淘汰计划核查报告）；吉尔吉斯斯坦（最终淘汰管理计划进度报告）；圣多美和普林西比（最终淘汰管理计划核查报告）。

文件结构

3. 秘书处将进度报告归类分为六节：

第一节：	国家淘汰计划和最终淘汰管理计划
第二节：	行业淘汰计划
第三节：	体制建设
第四节：	为了气候共同利益调动资源
第五节：	消耗臭氧层物质销毁项目
第六节：	氟氯烃示范和投资项目

一. 国家淘汰计划和最终淘汰管理计划

4. 开发计划署、环境规划署、工发组织和世界银行提交了下列报告：

(a) 巴西：国家氟氯化碳淘汰计划（2010 年核查报告、2011 年进度报告和 2012 年行动计划）（开发计划署）

(b) 布基纳法索：最终淘汰管理计划核查报告（2008 年）（环境规划署）

(c) 科特迪瓦：最终淘汰管理计划核查报告（2007-2008 年）（环境规划署）

(d) 印度尼西亚：国家淘汰计划（2007-2008 年运行情况核查）（开发计划署）

(e) 吉尔吉斯斯坦：最终淘汰管理计划进度报告（第三次亦即最后一次付款）（环境规划署）

(f) 菲律宾：国家氟氯化碳淘汰计划 （2009 和 2010 年核查报告及 2012 年行动计划）（环境规划署）

(g) 圣多美和普林西比：最终淘汰管理计划核查报告（2007-2009 年）（环境规划署）

5. 秘书处结合最初的项目提案、有关国家政府依据《蒙特利尔议定书》第 7 条报告的消耗臭氧层物质数据、之前提交执行委员会的进度报告和执行委员会及缔约方大会做出的相关决定，审查了已提交的报告。

巴西：国家氟氯化碳淘汰计划（2010 年核查报告、2011 年进度报告和 2012 年行动计划）（开发计划署）

6. 执行委员会第三十七次会议核准了在 2010 年 1 月 1 日之前巴西全部淘汰氟氯化碳消费的国家淘汰计划，原则上核准供资金额 26,700,000 美元。执行委员会第五十九次会议核准了国家淘汰计划第八次亦即最后一次付款。委员会还请在提交 2010 年消费核查报告之前每年都核查巴西国家氟氯化碳淘汰计划。在第六十三次会议上，执行委员会请巴西政府在国家淘汰计划完成之前，在开发计划署协助下，向执行委员会每年的第一次会议提交上一年年度执行报告。开发计划署第六十六次会议提交了 2010 年消费核查报告、2011 年进度报告以及 2012 年年度执行计划。

核查报告

7. 核查报告表明巴西满足了巴西政府与执行委员会关于 2010 年淘汰氟氯化碳的协定要求。2010 年，巴西的氟氯化碳进口量为零、出口量为 13.8 ODP 吨。

2011 年进度报告

8. 在制冷维修行业分发了大部分已购买的成套工具。一家回收中心在巴西南部地区（阿雷格里港）运营，最后一个储存设施已经建立。2011 年安装了 47 套回收设备，因此总数达到 95 套，还有 25 套没有安装。挑选两栋公共建筑物接受无氟氯化碳冷水机，采购投标过程已经启动。挑选 4 家企业用以示范商用制冷设备的改造或更换，已经启动了采购过程。最后，分发一部关于由使用氟氯化碳的计量吸入器转向替代品的纪录片，并且编写了小册子。

2012 年年度执行计划

9. 2012 年，计划开展一些活动以完成国家淘汰计划：为巴西北部剩余的 25 套 CFC-12 再循环设备确定并试运行设备，为技师分发也可用于氟氯烃和某些氢氟碳化物的回收工具、委托更换两栋公共建筑物的冷水机；改造或更换另外 18 套商用 CFC-12 设备；最后确定氟氯化碳排放限制技术标准；改进氟氯化碳控制系统国家贸易模块，以列入地方回收、再循环和再生制冷剂的跟踪工具；以及在业务和财务上结束项目。

秘书处的评论

核查报告

10. 核查报告中提交的数据与巴西向臭氧秘书处提交的第 7 条消费数据一致。

核定资金和余额

11. 截至 2011 年 12 月，除 1,808,548 美元（7%）外的所有供资都已拨付。开发计划署报告说，剩余资金已经承付给国家淘汰计划活动。两项活动与氟氯烃活动可能形成协同增效，但与其相关的氟氯烃淘汰活动不会产生，即氟氯化碳排放/废气控制措施，以及改进

源于回收的库存管理。可能的话第六十四次会议上核准的巴西氟氯烃淘汰管理计划将这些协同增效考虑在内。

2012 年年度执行计划

12. 秘书处还请进一步介绍为商用制冷行业中的中小企业采购的设备情况。开发计划署通知说，设备将以无消耗臭氧层物质技术为基础。

13. 秘书处注意到，进度报告还提供了 HCFC-22 和氟氯化碳回收和再循环中心以及再生中心的数据，表明 2011 年各中心处理的 CFC-12 和 HCFC-22 数量少于 2009 年。再生中心处理的 CFC-12 数量似乎从 2010 年的 4.8 吨减至 2011 年的 2.9 吨 ，而 HCFC-22 数量从 2010 年的 16.9 吨增至 2011 年的 27.4 吨。CFC-12 回收率降低，可能是因为更换了使用氟氯化碳的制冷设备以及使用 CFC-12 的大型工业设备物主似乎在为了维护目的而囤积各类氟氯化碳。氟氯烃的回收和再生率提高，与巴西政府根据氟氯烃淘汰管理计划对氟氯烃消费量增长实行限制有关。HCFC-22 的原价提高了约 30%至 40%，因此，HCFC-22 的制冷剂回收和再生业务在经济上更加可行。

14. 开发计划署根据一项提供详细情况的请求进一步介绍了 2012 年的规划活动在何种程度上能够有助于维持各类氟氯化碳的零消费并促进巴西淘汰氟氯烃。巴西仅通过 RRR 结构（更换设备、回收、再循环和再生活动）供应氟氯化碳。这种结构在物主有（经济或技术）能力更换或改造使用氟氯化碳的设备之前为设备提供了高质量的再循环/再生氟氯化碳。从更换冷水机和小型商用设备中回收的各类氟氯化碳可以再循环，这不仅是为了确保平稳过渡和减轻非法贸易风险，而且是为了向排放高全球变暖潜势的氟氯化碳提供符合成本效益的替代品。安装的 RRR 结构也可以处理氟氯烃和某些氢氟碳化物。最后确定商用制冷行业氟氯化碳排放限制技术标准，也将包括氟氯烃的排放限制。改进“氟氯化碳国家贸易模块”将为回收、再循环和再生制冷剂提供一个跟踪工具。该工具对国家贸易进行监测，向主管当局及时提供信息，经过推广还可以监测氟氯烃和氢氟碳化物。

秘书处的建议

15. 谨建议执行委员会考虑：

(a) 注意到巴西国家氟氯化碳淘汰计划（国家淘汰计划）2010 年核查报告和 2011 年年度执行报告；

(b) 核准 2012 年年度执行计划；

(c) 请开发计划署考虑继续报告巴西国家淘汰计划的执行进度，同时按照议程项目 7（d）下讨论结果规定的格式和时间表提供此类其他报告；以及

(d) 请巴西政府和开发计划署在国家淘汰计划完成后，按照第六十五次会议上指出的格式提交一份项目完成报告。

布基纳法索：最终淘汰管理计划核查报告（2008 年）（环境规划署）

背景

16. 环境规划署作为牵头机构代表布基纳法索政府根据第 45/54（d）号决定提交了布基纳法索 2008 年氟氯化碳消费情况核查报告。执行委员会第五十次会议核准了布基纳法索的最终淘汰管理计划，到 2009 年 1 月 1 日全部淘汰氟氯化碳消费。供资总额 345,000 美元，外加 23,400 美元机构支助费用给环境规划署、21,450 美元机构支助费用给加拿大政府，原则上获得执行委员会的核准，并在执行委员会第五十次和第五十四次会议上分两次付款发放给每个机构。

核查报告

17. 核查表明，2008 年，布基纳法索没有消费氟氯化碳，消耗臭氧层物质许可证制度运行良好。核查发现 HFC-134a 和 HCFC-22 的消费量正在增长。报告指出，布基纳法索在管制消耗臭氧层物质方面实行强硬而有效的监管，自 2006 年 1 月以来，涉及西非经济和货币联盟（西非经货联盟）（布基纳法索、贝宁、科特迪瓦、冈比亚、马里、塞内加尔和多哥）的次区域管理条例也已经生效，该管理条例禁止进口和出口附件 A、B 和 E 的所有物质及含这些物质的设备。

<u>秘书处的评论</u>

18. 布基纳法索政府依据《蒙特利尔议定书》第 7 条报告的 2008、2009 和 2010 年各类氟氯化碳的消费量为零。

19. 环境规划署通知秘书处，西非经货联盟管理条例还未经修正以禁止氟氯烃，但该管理条例目前允许对进口氟氯烃和使用氟氯烃的设备发放许可证。

20. 秘书处注意到，核查报告载有一项建议，分析现行的管理条例，以将氟氯烃和使用氟氯烃的设备考虑在内。环境规划署解释说，2013 年一项推出年度配额的新的管理条例草案已报请布基纳法索政府批准，因为现行的管理条例（国家和次区域一级）只要求发放进口许可证，但不限制允许数量。

<u>秘书处的建议</u>

21. 谨建议执行委员会：

(a) 注意到关于核查布基纳法索氟氯化碳消费情况和该国履行淘汰氟氯化碳消费义务情况的报告；以及

(b) 又赞赏地注意到布基纳法索报告自 2008 年以来《蒙特利尔议定书》第 7 条下的各类氟氯化碳消费量为零。

科特迪瓦：最终淘汰管理计划核查报告（2007-2008 年）（环境规划署）

背景

22. 环境规划署作为牵头机构代表科特迪瓦政府根据第 45/54（d）号决定提交了关于 2007 至 2008 年科特迪瓦氟氯化碳消费情况的核查报告。执行委员会第五十四次会议核准了科特迪瓦的最终淘汰管理计划，到 2009 年全部淘汰氟氯化碳消费量。供资总额 565,000 美元，外加机构支助费用 36,660 美元给环境规划署、21,225 美元给工发组织，原则上获得核准，并在执行委员会第五十四次和第五十八次会议上分两次付款发放给每个机构。

核查报告

23. 核查表明，科特迪瓦实现了 2008 年在国家一级减少消耗臭氧层物质消费量的总体目标。2008 年的消耗臭氧层物质实际消费量为 20 ODP 吨，而与执行委员会的协定规定最高允许消费量为 44.1 ODP 吨。核查发现 2007 年的消耗臭氧层物质消费量为 50 ODP 吨。科特迪瓦政府同该次区域其他国家一道通过了西非经货联盟管理条例。该国许可证制度运行良好，所涉政府机构进行了有效沟通。

秘书处的评论

24. 科特迪瓦政府依据《蒙特利尔议定书》第 7 条报告的 2007、2008、2009 和 2010 年的氟氯化碳消费量分别为 35.5、12.0、12.0 和零 ODP 吨。

25. 秘书处注意到依据第 7 条报告的 2007 和 2008 年数据与核查报告中的进口数据相差悬殊。核查报告中报告 2007 年的氟氯化碳消费量为 50 ODP 吨，而第 7 条下报告 35.5 ODP 吨；2008 年两个信息源报告的数据分别为 20.0 ODP 吨和 12.0 ODP 吨。环境规划署通知秘书处说，国家臭氧机构指出，核查报告所载的数据最精确，它已经同意纠正已经提交的第 7 条数据。科特迪瓦政府在环境规划署协助下，于 2011 年 3 月 15 日提交了一封正式信件，要求修改依据第 7 条报告的 2007 和 2008 年氟氯化碳消费数据。

秘书处的建议

26. 谨建议执行委员会：

(a) 注意到关于核查 2007 至 2008 年间科特迪瓦在最终淘汰管理计划下氟氯化碳消费情况和该国履行淘汰氟氯化碳消费方义务情况的报告，注意到该国报告 2010 年的各类氟氯化碳消费量为零。

(b) 注意到科特迪瓦政府请臭氧秘书处修改在第 7 条下报告的 2007 和 2008 年的氟氯化碳消费数据。

印度尼西亚：国家淘汰计划（2007-2008年运行情况核查）（开发计划署）

背景

27. 执行委员会第四十四次会议核准了印度尼西亚的国家淘汰计划，开发计划署担任牵头执行机构，工发组织和世界银行担任合作执行机构，在2008年1月1日前全部淘汰各类氟氯化碳、四氯化碳和三氯乙酸的受控用途。印度尼西亚的国家淘汰计划综合了若干项之前的行业计划和新活动，并在国家一级推出了消费核查。为国家淘汰计划活动核准的资金在第三十七次至第五十四次会议上分六次付款，总额为20,645,507美元，外加1,754,701美元机构支助费用。

核查报告

28. 2009年7月至8月开展的核查表明，印度尼西亚在国家一级实现了2007和2008年消耗臭氧层物质消费方面的总体目标，2007和2008年的消耗臭氧层物质实际消费量分别为202.56 ODP吨和近3.32 ODP吨。2008年所有行业（泡沫塑料、汽车空调维修、制冷制造、制冷维修、气雾剂和溶剂）都达到了消耗臭氧层物质消费目标，2007年除汽车空调行业外的所有其他行业也达到了该目标。另据报告，与各行业相关的政策和监管行动以及提高意识行动都得到了充分贯彻。

<u>秘书处的评论</u>

29. 执行委员会核准了印度尼西亚国家淘汰计划的最后一次付款，在这么做时提出一项保留，即开发计划署作为牵头执行机构将代表该国政府继续提供该协定剩余期限，即2010年之前各年份氟氯化碳消费情况的年度报告和核查报告。2009和2010年的核查报告目前还没有提交；2008、2009、2010和2011年年度执行报告也是如此。开发计划署指出，印度尼西亚禁止进口各类氟氯化碳、四氯化碳、三氯乙酸和哈龙，此项禁令自2008年1月1日起生效，比《蒙特利尔议定书》时间表提前，2008年完成的核查证实执行委员会协定的条款得到遵守。印度尼西亚依据《蒙特利尔议定书》第7条提交的数据表明，2008、2009和2010年的消耗臭氧层物质（除氟氯烃以外）消费量为零。开发计划署指出，除监测外，2009和2010年没有开展过实质性活动，剩余预算16,000美元编入2012年最后活动方案中。

30. 秘书处指出，由于海关数据（0 ODP吨）、贸易部的信息（0 ODP吨）和统计局的信息（3.32 ODP吨）有差异，所以核查员只能核查2008年的消费量大概是或低于3.32 ODP吨。统计局的数据是在28个海关提供给该署的书面和电子海关记录的基础上产生的。核查员分析了这一问题，确认差异似乎源于所提供的书面记录。秘书处向开发计划署指出，印度尼西亚政府依据第7条报告的2008年的各类氟氯化碳消费量零，并请予以澄清。开发计划署解释说，核查员使用了不同来源的可比数据，根据印度尼西亚中央统计局的数据，确认进口量为3.32 ODP吨，而其他两个数据源没有发现进口；然而，如果数据有差异，一般要求政府使用海关数据作为更可靠的数据源，后者显示消费量为零。这样，第7条数据仍然为已经报告过。

31. 核查证实，印度尼西亚遵守了政府与执行委员会关于印度尼西亚淘汰各类氟氯化碳的协定规定，该国2007和2008年的消费量低于协定中具体规定的最大允许消费量。

秘书处的建议

32. 谨建议执行委员会：

(a) 注意到关于印度尼西亚 2007-2008 年消耗臭氧层物质消费情况的核查报告；

(b) 请开发计划署代表印度尼西亚政府向第六十八次会议提交 2009 和 2010 年核查报告；以及

(c) 请开发计划署按以下要求报告印度尼西亚国家淘汰计划的执行进度：

(一) 2008 至 2011 向第六十七次会议报告，以议程项目 7（d）下进行的讨论结果规定的格式提供报告；以及

(二) 2012 年及以后年份，以议程项目 7（d）下进行的讨论结果规定的格式和时间表提供此类其他报告。

(d) 请印度尼西亚政府和开发计划署在国家淘汰计划完成后按照第六十五次会议上指出的格式提交项目完成报告。

吉尔吉斯斯坦：最终淘汰管理计划进度报告（第三次亦即最后一次付款）（环境规划署）

33. 执行委员会第五十次会议原则上核准吉尔吉斯斯坦的最终淘汰管理计划，总价值为 550,000 美元，54,065 美元机构支助费用给作为执行机构的开发计划署和环境规划署。所有预见的供资在第五十次、第五十五次和第六十次会议上分三次付款核准。在第六十次会议上，请吉尔吉斯斯坦政府提交一份关于与最终淘汰管理计划第三次亦即最后一次付款相关的工作方案的报告。

进度报告

34. 自 2010 年 4 月核准第三次付款以来，吉尔吉斯斯坦为全国举办了一些讲习班和研讨会，包括：2010 年 3 期回收和再循环讲习班（92 名学员）；2010 和 2011 年 5 期关于制冷方面最佳做法的讲习班（115 名学员）；9 期为海关官员和环境视察员提供培训的讲习班（265 名受训员）；和 2010 年在医院举办的 7 期关于计量吸入器的讲习班（261 名学员）。此外，吉尔吉斯斯坦的 77 名海关官员参加了该国与欧洲和中亚合作实施项目举行的两期区域讲习班。购置并向国家制冷协会提供了一套回收设备和一套多气体分析仪。

秘书处的评论

35. 吉尔吉斯斯坦依据 2010 年《蒙特利尔议定书》第 7 条报告的各类氟氯化碳消费量为零。截至 2011 年 12 月，为最终淘汰管理计划核准的所有经费都已拨付。

36. 在第六十三次会议上，秘书处注意到，吉尔吉斯斯坦氟氯烃淘汰管理计划第一阶段最初的重点是确保供应额外的制冷剂回收设备和工具，以支持技师培训工作，因为估计具备充足的基本再循环能力的技师不足 50%（UNEP/OzL.Pro/ExCom/63/37 号文件）。对于秘书处提出的 2010 和 2011 年在最终淘汰管理计划方面开展的活动是否改善了这一状况，环境规划署答复说，除最终淘汰管理计划下最后一轮采购期购买的设备以外，同现在供应的先进工具相比，大多数已购设备现已过时。执行机构通知说，作为氟氯烃淘汰管理计划

的一部分，某些中心将实现现代化；目前氟氯烃淘汰管理计划下的供资不足以使所有中心升级。

37. 环境规划署对吉尔吉斯斯坦的 CFC-12 回收和再循环做了一些澄清（见表 1）。在吉尔吉斯斯坦回收的总共 18,973 公斤各类氟氯化碳中，6,455 公斤由再生和再循环中心在 2003 至 2011 年累积进行再循环。

表 1：吉尔吉斯斯坦回收和再循环的各类氟氯化碳数量

年份	回收和再利用（现场过滤）（公斤）	由再生和再循环中心再循环和净化（公斤）
2003	750	0
2004	2864.6	1101.9
2005	3930.8	1501.4
2006	1569.8	1013.7
2007	1900	588
2008	2142.8	700
2009	2734	843
2010	1939	707
2011	1142	186
共计	18,973	6,455

38. 吉尔吉斯斯坦国家臭氧机构证实该国有 5 套再生和再循环设备。2003 年通过制冷剂管理计划活动购买的 3 套设备只能再循环各类氟氯化碳，而在执行最终淘汰管理计划期间购买的另两套设备可以再循环各类氟氯化碳和氟氯烃。目前，由于原生物质 HCFC-22 费用仍然非常低而缺乏动力，吉尔吉斯斯坦没有再循环氟氯烃。

秘书处的建议

39. 谨建议执行委员会：

(a) 注意到关于与吉尔吉斯斯坦最终淘汰管理计划第三次亦即最后一次付款相关的 2010-2011 年工作方案的报告；

(b) 请环境规划署继续报告吉尔吉斯斯坦最终淘汰管理计划的执行进度，同时以议程项目 7（d）下进行的讨论结果规定的格式和时间表提供此类其他报告；以及

(c) 请吉尔吉斯斯坦政府和环境规划署在最终淘汰管理计划完成后，按照第六十五次会议上指出的格式提交一份项目完成报告。

菲律宾：国家氟氯化碳淘汰计划（2009 和 2010 年核查报告和 2012 年行动计划）（环境规划署）

背景

40. 2002 年 11 月，执行委员会第三十八次会议原则上核准了菲律宾的国家氟氯化碳淘汰计划（国家淘汰计划），总价值为 10,575,410 美元、机构支助费用 896,788 美元，以淘汰各类氟氯化碳 2,017.6 ODP 吨。同一次会议上商定了第一次付款 3,010,873 美元和机构

支助费用 259,979 美元。第四十一次、第四十四次、第四十七次、第五十一次和第五十四次会议核准了随后的付款，以资助 2003 至 2008 年的各项活动。

41. 在第六十五次会议上，执行委员会核准了将国家淘汰计划下的其余活动从世界银行转到环境规划署。第 65/10（e）号决定特别列入，世界银行将国家淘汰计划的剩余资金退回第六十六次会议，菲律宾政府要在环境规划署协助下向第六十六次会议提交一份关于 2009 和 2010 年氟氯化碳消费情况的核查报告和 2012-2013 年国家淘汰计划下的剩余资金的执行计划。

核查报告

42. 根据实际进口量核查的 2009 年和 2010 年氟氯化碳消费量分别为 208.64 和零 ODP 吨，而 2009 和 2010 年的最大允许消费量分别为 300 和零 ODP 吨。《蒙特利尔议定书》第 7 条下报告的数据表明，该国 2009 和 2010 年的氟氯化碳消费量分别为 208.64 ODP 吨和 0 ODP 吨。

进度报告

43. 同第六十五次会议上提供的信息比较，没有开展或完成新活动，而 2011 年 9 月之前的累积进度报告已经提交。报告中唯一增加的项目涉及一名顾问 2011 年 10 月的来访，以为氟氯烃淘汰管理计划最后确定沫塑料行业计划的项目编制。

44. 到 2011 年年底，该项目拨付了为国家淘汰计划核准的 10,575,410 美元中的 82%（8,671,836 美元）。在第六十六次会议上，剩余资金（1,878,851 美元）将转给作为新的执行机构的环境规划署。

2012 年 4 月至 2013 年 12 月的执行计划

45. 环境规划署代表菲律宾政府提交了关于该项目剩余资金的执行计划，以便维持该国的各类氟氯化碳淘汰并确保消费量继续保持为零 ODP 吨。其中大多数活动是在延续前几年发起的活动，并且包括：

(a) 继续监测赠款受援国和国家淘汰计划中所列的其他企业（泡沫塑料和制冷企业）以确保其履约；

(b) 向维修技师培训中心交付设备，包括继续支持技师认证工作以列入氟氯烃设备维修；

(c) 继续为汽车空调视察提供技术援助，以通过为视察现场提供制冷剂识别器继续执行带 CFC-11 汽车空调的机动车的禁令；

(d) 制定管理信息系统，将参与国家淘汰计划执行的不同机构联系起来，以监测活动进展情况；

(e) 完成凭证制度并为适当维修冰箱和空调机分配其余工具和设备，以及最后确定该系统的技术稽核；

(f) 向区域环境管理局各办公室增加业务支持，以确保在维修行业开展全国性活动；

(g) 通过提供信息联系加强区域机构间合作和协调；

(h) 为再生设施提供其余工具并执行消耗臭氧层物质废物再生计划；

(i) 继续提高意识；以及

(j) 继续开展项目管理机构的业务以协调上述活动。

46. 菲律宾政府在其呈件中要求主管当局在 2013 年 12 月前继续完成国家淘汰计划下的所有项目并承诺在此时限之前为该项目全额支付其余资金。

47. 下文表 2 汇总了 2012-2013 年执行计划的预算（详细预算后为附件一），并且包括为 2011 年 7 月至 12 月产生的费用追加供资 43,080 美元所申请的金额：

表 2：拟议工作计划和预算汇总表

2012 年 4 月至 2013 年 12 月	**预算（美元）**
项目管理	604,172
防止额外供应消耗臭氧层物质/氟氯烃	259,525
消除该国的氟氯化碳需求	510,823
管理无用的消耗臭氧层物质	198,593
信息、教育和通信及提高公众意识	305,738
共计	1,878,851

秘书处的评论

48. 秘书处审查了菲律宾政府按照国家淘汰计划之前的工作计划并对照该国继续进行氟氯化碳淘汰工作所需要的其余行动通过环境规划署提交的工作计划。根据其 2010 年第 7 条数据和其提交的核查报告来看，菲律宾已经实现了《蒙特利尔议定书》规定的氟氯化碳履约目标。考虑到国家淘汰计划的资金还剩下近 20%的余额（见上文第 44 段），鉴于该工作计划没有牵涉到消耗臭氧层物质淘汰目标，应当逐项监测活动进展情况，具体来讲即执行委员会确认并商定的活动的进展情况。

49. 秘书处注意到，所列的大多数活动都是 2007 至 2009 年国家淘汰计划之前的工作计划中未完成的活动，并非所有举措都将氟氯烃淘汰活动，特别是维修行业中的活动（如培训和维修技师工作）考虑在内。秘书处同样提请环境规划署注意以下事实，尽管需要开展活动以维持各类氟氯化碳的零消费，但执行委员会已经非常明确地表明，其余的氟氯化碳淘汰资金应当考虑将促进淘汰氟氯烃的活动。秘书处表示关切的还有，目前拟议的 2012 和 2013 年工作计划中提及氟氯化碳淘汰的许多活动没有明确依据。

50. 环境规划署在答复中告知秘书处，由于拨款困难且早先同世界银行签署的赠款协定已终止，因此活动仍然没有完成，菲律宾在执行过去规划的某些活动方面出现一些拖延。转给新的执行机构也必然要求财务和执行安排有所调整，这进一步加剧了这种状况。环境规划署还指出，目前的工作计划考虑到菲律宾在氟氯化碳淘汰工作中同其伙伴所做的财务承诺，这需要兑现，因为这些伙伴与氟氯烃淘汰工作中的伙伴相同。

51. 秘书处根据所提供的理由，提议现在的工作计划能够兑现对今后 12 个月的近期承诺，但低于上文表 2 提议的金额，包括申请的追加供资。它还提请环境规划署注意以下事实，菲律宾的氟氯烃淘汰管理计划总体战略仍然没有得到落实，并告知菲律宾政府应当在

考虑到国家淘汰计划剩余资金的情况下加速其完成工作，同时认真考虑如何将这些资金纳入氟氯烃淘汰管理计划，尤其是维修行业。可以在执行委员会核准未来的年度执行工作计划后考虑拨付剩余资金。如下文表 3 所示，菲律宾政府和环境规划署提交了今后 12 个月的订正预算：

表 3：商定的 2012 年 4 月至 2013 年 4 月工作计划和预算

2012 年 4 月至 2013 年 4 月	预算（美元）
防止额外供应消耗臭氧层物质/包括氟氯烃	65,000
继续在维修行业开展工作（防止额外的氟氯化碳需求，包括氟氯烃）	170,000
管理无用的消耗臭氧层物质	30,000
提高意识和信息传播	20,000
项目管理机构	143,550
小计	428,550
追加供资（2011 年 7 月至 2011 年 12 月）	43,080
共计	471,630

<u>秘书处的建议</u>

52. 谨建议执行委员会考虑：

(a) 注意到：

(一) 关于核查菲律宾 2009 和 2010 年氟氯化碳消费情况和该国履行淘汰氟氯化碳消费义务情况的报告；

(二) 菲律宾依据《蒙特利尔议定书》第 7 条报告的 2010 年各类氟氯化碳消费量为零；

(三) 环境规划署代表菲律宾政府提交的国家氟氯化碳淘汰计划下的 2012 年 4 月至 2013 年 4 月年度执行计划，核准其中所载的同期拨款至多 471,630 美元所涉及的活动，并请环境规划署在第七十次会议上按照议程项目 7（d）下进行的讨论结果规定的格式向执行委员会提交一份年度进度报告；以及

(b) 请菲律宾政府通过环境规划署在执行委员会第六十八次会议之前为剩余资金 1,407,221 美元提交一份随后的年度工作计划，同时考虑到剩余资金应考虑到在该国的氟氯烃淘汰管理计划范围内促进淘汰氟氯烃的各项活动。

圣多美和普林西比：最终淘汰管理计划核查报告（2007-2009 年）（环境规划署）

背景

53. 环境规划署作为牵头机构代表圣多美和普林西比政府按照第 45/54（d）号决定提交了 2007-2009 年圣多美和普林西比氟氯化碳消费情况核查报告。执行委员会第五十四次会议核准了圣多美和普林西比的最终淘汰管理计划，到 2009 年全部淘汰氟氯化碳消费。执行委员会原则上核准了供资总额 190,000 美元，外加机构支助费用 9,750 美元给环境规划署、10,350 美元给工发组织，并在执行委员会第五十四次和第五十七次会议上分两次付款发放给两个机构。

核查报告

54. 核查表明，圣多美和普林西比执行有效的许可证制度并拥有强有力的国家臭氧机构。2008 和 2009 年国家一级的消耗臭氧层物质消费总体目标已经实现。2008 年消耗臭氧层物质的实际消费量为 0.2 ODP 吨（协定规定的最大允许消费量为 0.7 ODP 吨），2009 为零（协定规定的最大允许消费量为 0.7 ODP 吨）。

秘书处的评论

55. 圣多美和普林西比政府依据《蒙特利尔议定书》第 7 条报告的 2008 年氟氯化碳消费消费量为 0.2 ODP 吨，2009 和 2010 年的消费量为零。圣多美和普林西比的许可证和配额制度也适用于附件 A 和附件 C 中的各类物质。这些物质的年度配额由环境部和贸易部共同颁布。

秘书处的建议

56. 谨建议执行委员会：

(a) 注意到关于核查圣多美和普林西比 2007 至 2009 年间氟氯化碳消费情况和该国履行淘汰氟氯化碳消费义务情况的报告；以及

(b) 进一步注意到圣多美依据《蒙特利尔议定书》第 7 条报告的 2009 和 2010 年各类氟氯化碳消费量为零。

二. 行业淘汰计划

57. 开发计划署和世界银行提交了下列报告：

(a) 中国：中国溶剂行业淘汰消耗臭氧层物质情况（2010 年进度报告、2009 和 2010 年运行情况核查和 2010 年三氯乙酸技术核查）（开发计划署）

(b) 印度：关于 2010 年间消费和生产行业四氯化碳淘汰计划执行情况的报告（世界银行）

中国：中国溶剂行业淘汰消耗臭氧层物质情况（2010 年进度报告、2009 和 2010 年运行情况核查和 2010 年三氯乙酸技术核查）（开发计划署）

58. 开发计划署作为执行机构代表中国政府提交了中国淘汰消耗臭氧层物质溶剂行业计划 2009 和 2010 年年度进度报告、2009 和 2010 年三氯乙酸受控用途消费情况核查报告以及三家受益企业作为样本的淘汰技术核查报告，供执行委员会第六十六次会议审议。

背景

59. 执行委员会第三十次会议核准了中国的溶剂行业计划，费用总额为 5,200 万美元，外加支助费用给开发计划署。资金已得到核准，分为 2000 至 2010 年执行年度 11 次年度付款，最后一次付款在第五十九次会议上核准。

60. 淘汰工作是通过针对具体企业的投资活动和通过凭证制度管理的面向小企业的技术援助方案共同实现的。通过监管生产和进口维护消费限制。减少生产受关于各类氟氯化碳和四氯化碳的中国生产行业淘汰计划管制。自 2003 年 6 月 1 日起禁止使用四氯化碳作为溶剂，自 2006 年 1 月 1 日起禁止使用 CFC-113 作为溶剂；因此，在过去若干年里相关活动已经完成。该计划将涉及中国使用三氯乙酸作为最后的消耗臭氧层物质溶剂，这种用途将在 2010 年 1 月 1 日前全部淘汰。

投资项目和活动的淘汰

企业一级的活动

61. 依据溶剂行业计划，2010 年记录的减少量是通过 2008 和 2009 年启动的、旨在淘汰三氯乙酸用作溶剂的消耗臭氧层物质减少合同项目下的企业淘汰活动的完成实现的。2009 年开展的各项活动最终减少了总共 73.7 ODP 吨三氯乙酸，2010 年又减少了 3.7 ODP 吨。溶剂行业计划在 11 年里共淘汰了 247.07 ODP 吨三氯乙酸消费量。在以往各年，替代 CFC-113 的活动导致累积减少了 2,689.5 ODP 吨，与四氯化碳相关的活动导致淘汰了 29.5 ODP 吨。淘汰是通过 379 份单独合同实现的。下文表 4 列示了 2009 和 2010 年消费量减少情况以及行业计划下计划淘汰与实现的减少量的比较情况：

表 4：消费量减少情况（2009 和 2010 年）与中国溶剂行业计划下计划淘汰情况

按 ODP 吨计量的物质		CFC-113	三氯乙酸	四氯化碳	共计
2009 年		0	73.7	0	73.7
2010 年		0	3.7	0	3.7
2000-2010 年总量	计划	3,300	537	110	3,947
	企业累积减少量	2,689.5	247.1	29.5	2,966.1
	份额（企业/计划的累积减少量）	81.5%	46.0%	26.8%	75.1%
	消费的实际减少量	3,300	537	110	3,947

62. 报告指出了实际消费减少量，即国家一级的淘汰量与企业的累积减少量存在差别的原因，这在淘汰计划中得到讨论。一个原因是，一些企业似乎通过其自身的活动而不是项

目供资消除了三氯乙酸消费。第二，许多企业没有资格获得供资，即外资企业虽然在消费消耗臭氧层物质溶剂，但没有资格领取该计划下的供资。

技术援助活动

63. 在该行业计划下，前几年开始的一些技术援助活动在继续进行。这包括与制止消耗臭氧层物质非法进口、生产和使用有关的活动，其中包括 2010 年最后确定新的“消耗臭氧层物质进出口管理办法”草案、为地方政府办公室举办培训讲习班和调查非法消费情况；两项具体调查正在研究四氯化碳和 CFC-113 使用情况。还继续开展地方环保局的能力建设活动，以便利并加强履行《蒙特利尔议定书》义务的监测工作。在溶剂行业计划下开展的活动所针对的 18 个省市中，2009 年收到了 12 个城市的报告。在制止消耗臭氧层物质非法贸易的能力建设活动中，已经为海关印制了培训材料和宣传材料。最后，开展了一项详细的技术核查并将核查报告提交本次会议。

64. 在溶剂行业计划下还开展了一些公众意识和培训活动。这包括臭氧日与溶剂行业有关的活动、对中国地方当局的政策培训、地方行政机构遵照《蒙特利尔议定书》进行的培训和交流能力建设以及网络设备和会议设施的相关支助。最后，拟定了一些政策和管理条例，其中有在 2010 年 1 月 1 日前全国禁止生产三氯乙酸（从而消除了消费）并在 2011 年 1 月 1 日禁止企业使用三氯乙酸。

65. 活动核查表明已经开展了相关活动。消费核查证实，2009 和 2010 年溶剂行业的四氯化碳、三氯乙酸和 CFC-113 使用量为零。2010 年全部用尽了剩余供资，而 2009 年年底的期初费用总额为 6,824,620 美元，该项目账户上未留下余额。

<u>秘书处的评论</u>

66. 2009 年 11 月举行的第五十九次会议核准了一些将要开展的活动，当时的剩余资金金额为 700 多万美元。2010 年，开发计划署代表中国政府实施这些活动并承付剩余的项目资金。

67. 开发计划署代表中国提交的呈件对该计划下的活动、2009 和 2010 年取得的成果以及该计划开始时的情况进行了精彩而极其详细的概述。2009 和 2010 年提交的核查报告足以使人们对所提供信息的正确性充满信心。溶剂行业计划的执行工作已经完成。

<u>秘书处的建议</u>

68. 谨建议执行委员会：

(a) 注意到中国淘汰消耗臭氧层物质溶剂行业计划 2009/2010 年进度报告；以及

(b) 注意到 2009 和 2010 年相关的三氯乙酸核查报告。

印度：关于 2010 年间消费和生产行业四氯化碳淘汰计划执行情况的报告（世界银行）

69. 世界银行作为牵头执行机构代表印度政府向第六十五次会议提交了 2010 年年度方案执行情况核查报告。针对该呈件，执行委员会在其第 65/10（j）号决定中注意到，在核查中，自 2005 年年初已将使用四氯化碳用于氯乙烯单体生产归类为原料，而在 2007 年生产氯乙烯单体中使用四氯化碳已经归类为第十九次蒙特利尔议定书缔约方会议（第 XIX/15 号决定）规定的加工剂用途。执行委员会还在该决定第（三）分段中请世界银行要求印度政府相应地更新依据《蒙特利尔议定书》第 7 条报告给臭氧秘书处的 2008 至 2010 年的四氯化碳消费数据。同一项决定第（四）分段请世界银行与印度政府协调，调查在多大程度上 2008、2009 和 2010 年销毁的四氯化碳数量将抵消 2008、2009 和 2010 年为生产氯乙烯单体用作加工剂的四氯化碳数量，并提出一份相关报告以便最迟在第六十六次会议八周前提交。

70. 第六十五次会议之后，第二十三次缔约方会议讨论了四氯化碳普遍用作加工剂，具体用于生产氯乙烯单体的问题。第 XXIII/7 号决定“使用受控物质作为加工剂”第（8）段指出，缔约方“在 2012 年 12 月 13 日之前将在例外情况下为了推算生产和消费水平将四氯化碳用于生产氯乙烯单体视为原料用途”。前述决定使得执行委员会第 65/10（j）号决定第（三）和第（四）分段过时。

71. 第 65/10（j）（五）号决定请世界银行为第六十六次会议及时提供关于 2010 年间消费和生产行业四氯化碳淘汰计划的执行情况报告，可行的话提供计划活动的订正情况。世界银行提交的报告指出，2011 年 3 月对 2010 年的四氯化碳生产和消费进行了技术核查稽核。世界银行启用了一支独立稽核队对 4 家四氯化碳生产商、8 家二氯菊酰氯生产商、1 家氯乙烯单体和 1 家二氟苯甲酮工厂和坎德拉的 3 家储存设施进行了实地考察和文件审查。2010 年，臭氧机构没有发布向非原料用户销售的配额。稽核队证实，没有向非原料用户直接销售，四氯化碳生产商也没有进口或出口四氯化碳。因此，独立稽核队核实，它认为印度履行了《蒙特利尔议定书》规定的义务。2010 年 12 月，四氯化碳淘汰计划向四氯化碳生产商提供了最后一次亦即最终付款（210 万美元）。2011 年，国家臭氧机构在技术援助部分下开展了一些讲习班和培训活动。

72. 世界银行通知秘书处，剩余资金达 140 万美元，建议承担以下方面的费用：培训使用四氯化碳的产业集群和协会使用替代溶剂（400,000 美元）；制定和执行一项宣传战略以避免使用氯化碳并防止用户倒退（290,000 美元）；培训邦政府官员和污染控制委员会官员（196,000 美元）；为海关官员举办培训讲习班（196,000 美元）；编写成功事例出版物（38,000 美元）；以及持续进行项目管理机构的活动，包括监测（280,000 美元）。秘书处指出受控用途中的四氯化碳已经淘汰一年多了。它对同之前该行业计划下的活动相比以及同最初在氟氯烃淘汰管理计划下向第六十六次会议提交的为印度申请的海关培训相比发现有可能重复供资表示严重关切。秘书处还提出了为不同活动预见的供资金额相关的问题，并提出一些建议，包括增加一些活动以监测用于非受控用途的四氯化碳是否挪入受控用途，以及将资金转入其他活动，如氟氯烃淘汰管理计划。

73. 世界银行代表印度政府决定撤回呈件，因为分配供资的各种可能情况需要用更长时间来审议。尽管如此，秘书处认为，鉴于缔约方会议第 XXIII/7 号决定和第 65/10（j）（五）号决定要求向第六十六次会议报告，因此有必要将呈件提交执行委员会。

74. 谨建议执行委员会考虑：

(a) 注意到第二十三次缔约方会议第 XXIII/7 号决定第 8 段认为在 2012 年 12 月 31 日之前将在例外情况下为了推算生产和消费水平将四氯化碳用于生产氯乙烯单体视为原料用途，取代了执行委员会第 65/10（j）号决定第（三）和第（四）分段；

(b) 请世界银行向第六十九次会议提供关于印度为生产氯乙烯单体使用四氯化碳状况的 报告；

(c) 注意到关于 2010 年印度消费和生产行业的四氯化碳淘汰计划执行情况的报告和提供的相关核查；以及

(d) 请世界银行向第六十七次会议提供一份涉及印度四氯化碳淘汰计划剩余资金的工作计划。

三. 体制建设

关于朝鲜民主主义人民共和国体制建设项目的第 64/20 号决定的执行进度报告（环境规划署）

背景

75. 在第六十四次会议上，执行委员会决议将朝鲜民主主义人民共和国体制建设项目第六阶段的申请审议工作推迟到第六十六次会议，并请秘书处和作为执行机构的环境规划署向执行委员会第六十六次会议建议替代的拨款方法、组织结构和监测程序（第 64/20 号决定）。环境规划署提交了关于第 64/20 号决定执行情况的报告（附录一）。

关于替代的拨款方法、组织结构和监测程序的建议

76. 报告介绍了为该体制建设项目拨付资金的模式和以及 2011 年 11 月 28 日至 12 月 1 日环境规划署、朝鲜民主主义人民共和国国家环境协调委员会/国家臭氧机构和开发计划署进行的协商进程（平壤）。环境规划署亚太区域办事处和亚洲及太平洋经济社会委员会（亚太经社会）也进行了讨论。

77. 基于上述讨论的结果，后附报告（附录一）提出了一项建议，可以归纳如下：

<u>拨款</u>

- 环境规划署与国家环境协调委员会签署了一份财务协定以明确界定所有体制建设活动及各自的费用。
- 根据一项详细的年度工作计划，环境规划署通过开发计划署平壤办事处向国家臭氧机构以朝鲜元预付了资金
- 至迟在拟议活动前一个月，国家臭氧机构将提交一份详细的工作范围，报请环境规划署批准，以便为该项活动使用预付资金。

- 活动完成后两周，国家臭氧机构将提交一份在批准的工作范围内开展的活动的详细报告，包括支出报告及供环境规划署审查和监测的原始收据。
- 未经环境规划署提前批准而组织的任何活动不得由体制建设资金的预先付款来承担费用。

组织结构和监测程序

- 国家臭氧机构的工作人员将继续由政府聘任，并安排在环境和土地保护部内。

监测程序

- 根据环境规划署的程序要求所有国家提交的半年期进度报告。
- 预先批准的活动的工作范围。
- 完成后两周内提交的活动报告。
- 可能的话环境规划署的工作人员参与体制建设活动。
- 环境规划署履约援助方案将努力组织一年两次的考察，以进行审查和监督（国家环境协调委员会同意进入项目现场不受任何阻拦）。

秘书处的建议

78. 谨建议执行委员会：

(a) 注意到环境规划署提交的关于朝鲜民主主义人民共和国体制建设项目的执行委员会第 64/20 号决定执行情况的报告；以及

(b) 考虑拟议的替代拨款方法、组织结构和监测程序是否解决了执行委员会在其第六十四次会议上表达的关切。

四. 为气候共同利益调动资源

79. 在第六十三次会议上，执行委员会为四个独立的全球资源调动项目核准供资 680,000 美元，由开发计划署（200,000 美元）、环境规划署（100,000 美元）、工发组织（200,000 美元）和世界银行（180,000 美元）负责执行。这些项目旨在调动资源以实现仅通过氟氯烃淘汰便可以实现的气候惠益之外的共同利益。这些项目得到核准的条件是，将向第六十六次会议提交一份临时报告，其中包括一些规定的要素：增加拟议项目；透明度和善治以及管制现金流；保证这些项目将避免给各国提供不当的激励；探讨惠益分享的可能性，包括将资金返还多边基金；确保拟议项目的可持续性；避免类似项目的重复；交易成本方面的信息。请各机构向第六十九次会议提供关于项目的最后报告。核准的资金来自从泰国冷风机项目退回资金中拨出的、为未具体规定的项目保留的预算。

全球：为气候共同利益调动资源（开发计划署）

80. 开发计划署要完成的任务是制定制冷和空调制造行业的四个试点示范项目，审查技术干预措施以改进能效、国家政策和监管措施，从而维护这种干预措施，以便尽可能扩大将作为资源调动活动而资助的氟氯烃淘汰的气候影响。要求开发计划署在第六十七次会议

之前向执行委员会通报上述四项建议的情况，指出这仅是为了提供信息而提交的，这些建议不用多边基金供资。

进展情况

81.　开发计划署力图从双边和多边来源以及私营部门调动资源，并将用在企业、次级行业和行业一级。美利坚合众国已将 170 万美元转给开发计划署，用于在亚太区域国家选定的次级行业中展示和应用低全球变暖潜势和节能技术。开发计划署为全环基金印度尼西亚项目提案的编制提供了技术支持，侧重于资助空调和制冷行业中的能效改进工作。450 万美元的提案正在定稿准备提交，并将为在其他国家推广提供机会。开发计划署正在同其他双边捐助者继续共同努力，以为改善能效和低全球变暖潜势替代品调动资金。该机构还与私营部门技术提供者（泡沫塑料、空调和制冷行业）接触，以通过第 5 条国家的附属机构为低全球变暖潜势和节能型替代品带来额外投资。

秘书处的建议

82.　谨建议执行委员会注意到开发计划署提交的关于为气候共同利益调动资源的临时报告并重申第 63/20（a）（一）号决定，其中请开发计划署在第六十七次会议之前通报执行委员会上述四项建议的情况，指出这仅是为了提供信息而提交的，这些建议不用多边基金供资。

全球：与其他机构合作，调动资源以解决仅有维修行业的低消费量国家淘汰氟氯烃的气候共同利益问题（环境规划署）

83.　执行委员会核准为以下项目供资：关于筹资选择的研究、关于共同出资的区域讲习班、和/或针对一个或若干核准了氟氯烃淘汰管理计划的低消费量国家的一种或若干种共同出资试点用途。要求环境规划署确保在环境规划署履约援助方案下的网络会议中举办区域讲习班，以确保成本效益并确保讲习班的时间安排有助于把其他机构的资源调动活动的经验纳入其中。

进展情况

84.　已经草拟了关于筹资选择研究的工作范围，并且编辑了将参与研究工作的潜在专家顾问名单。参加区域讲习班的潜在受邀人员/伙伴初步名单已经拟定，履约协助方案小队计划在该网络范围及为 2012 年计划的专题会议范围内举办区域讲习班。将于 2012 年 4 月在布基纳法索为北非和西非法语国家举办的专题讲习班将讨论共同出资问题，环境规划署正在考虑低消费量国家的资源调动项目能否适用于该讲习班。

秘书处的建议

85.　谨建议执行委员会注意到环境规划署提交的关于与其他机构合作为仅有维修行业的低消费量国家淘汰氟氯烃落实气候共同利益的资源调动项目的临时报告。

全球：为淘汰氟氯烃和气候共同利益而调动资源（工发组织）

86. 执行委员会核准为编制两项关于可能为氟氯烃活动共同出资的项目提案而提供资金，但条件是，工发组织在第六十七次会议之前向执行委员会通报上述两项建议的情况，指出这将是仅为了提供信息而提交的，两项建议不用多边基金供资。

进展情况

87. 工发组织为渔业和食品加工业的两项试点转用项目确定了拉丁美洲和亚太区域的潜在国家。拟定的项目将分四个阶段执行：采用和调整现有可利用的办法以支助氟氯烃淘汰方面不符合供资条件的费用；确认并应用最有前途的替代技术以替代现有的设施并执行试点转换项目；监测转换技术的运行情况并评估节能情况；以及制定最有前途的财政计划以为类似设施的转换调动额外资金。

秘书处的建议

88. 谨建议执行委员会注意到工发组织提交的关于为淘汰氟氯烃和气候共同利益调动资源的项目的临时报告，并重申第 63/23（a）（一）号决定，其中请工发组织在第六十七次会议之前向执行委员会通报上述两项建议的情况，指出这仅是为了提供信息而提交的，这些建议不用多边基金供资。

全球：为淘汰烃氟氯共同利益研究项目调动资源（世界银行）

89. 执行委员会核准为专门研究碳额度货币化的研究项目提供资金。

进展情况

90. 世界银行编写了订正的概念说明，将项目重点放在在项目一级使用市场机制上，同时考虑到与 2011 年德班联合国气候变化大会上的碳融资相关的发展情况。此项研究将由一家咨询公司在世界银行监督下开展，将在 2012 年 12 月 31 日前完成，以便按照第 63/24 号决定向第六十九次会议提交最后报告。

秘书处的建议

91. 谨建议执行委员会注意到世界银行提交的关于为氟氯烃淘汰共同利益研究项目调动资源的临时报告。

五. 消耗臭氧层物质销毁项目

92. 第 58/19（a）（三）号和第 64/50 号决定请双边和执行机构每年向执行委员会第一次会议报告在项目核准后第一年开始的消耗臭氧层物质处置示范项目的进展情况和获得的经验，并在这些报告中列入以下方面的信息：收集或查明、运输、储存或销毁的各种消耗臭氧层物质的数量，财政、管理和共同出资安排以及任何其他相关问题。根据这些决定向第六十六次会议提交关于古巴和加纳正在进行的消耗臭氧层物质销毁项目的报告。

古巴：消耗臭氧层物质废物管理和处置试点示范项目的进度报告（开发计划署）

背景

93. 第六十二次会议核准了古巴的消耗臭氧层物质废物管理和处置的试点示范项目，总额为 525,200 美元，销毁总共 45.3 公吨消耗臭氧层物质废物，但条件是以后不为古巴的任何消耗臭氧层物质处置项目提供追加供资（第 62/27 号决定）。该试点项目试图为古巴消耗臭氧层物质的运输、储存和销毁制定一个有效且符合成本效益的后勤框架。

进展情况

94. 开发计划署与古巴于 2011 年 6 月签署了项目文件，还建立了所有利益攸关方均有参与的项目工作队。取得的进展包括：制定了所需的技术说明并确认了所需设备以使选中的设施适于进行消耗臭氧层物质销毁工作（2012 年将开始建造和组装该设施）；为各省的储存设施确认业务要求和设备；为消耗臭氧层物质的收集和运输设计专用卡车；以及订正法律框架以确保消耗臭氧层物质的销毁得到监管。

95. 实际的收集和销毁任务还没有启动，但一旦初步安排完成则开始试验。

<u>秘书处的评论</u>

96. 截至 2011 年 12 月，没有拨付任何资金，因为涉及到为建造该设施而调整的最初活动由古巴政府共同出资。

97. 目前，130 公吨的消耗臭氧层物质库存存放在区域仓库里。开发计划署指出，所有库存都是消耗臭氧层物质废物，不能再循环或回收。

<u>秘书处的建议</u>

98. 谨建议执行委员会：

(a) 注意到开发计划署提交的古巴的消耗臭氧层物质废物管理和处置试点示范项目的进度报告；以及

(b) 请开发计划署根据第 58/19（a）（三）号和第 64/50 号决定向执行委员会第六十九次会议提交关于古巴的试点示范项目的进展情况和获得的经验的报告。

加纳：消耗臭氧层物质废物管理和处置试点示范项目的进度报告（开发计划署）

背景

99. 第六十三次会议核准了加纳的消耗臭氧层物质废物管理和处置试点示范项目，总额为 198,000 美元，销毁总共 8.8 公吨消耗臭氧层物质废物。该项目与该国的氟氯烃淘汰管理计划和全球环境基金（全环基金）能效项目紧密地连成一体，使用寿命到期和提前退休的不节能冰箱将在区域仓库里收集和摧毁，以便回收消耗臭氧层物质。2011 年 5 月 9 日

收到了全环基金能效项目的供资（1,722,727 美元）确认书，这有助于为试点项目拨付资金（第 63/27 号决定）。

进展情况

100. 该项目下聘用的一名国际顾问出席了 2011 年 11 月 15 日至 16 日在阿克拉举行的全环基金能效项目第一期讲习班。出席该讲习班的有重要的公共和私人利益攸关方，这为该顾问提供了讨论以下方面相关问题的机会：分权的区域摧毁和回收中心；保留退休冰箱的记录；摧毁退休冰箱的安全工序；消耗臭氧层物质的回收、储存和运输；测试消耗臭氧层物质的构成；出口程序；保留记录和监管链；培训技师。处置项目、氟氯烃淘汰管理计划和全环基金能效项目密切协调极其重要，被视为对于消耗臭氧层物质稳定流动以进行收集处置必不可少。

101. 开发计划署蒙特利尔议定书事务股计划于 2012 年 4 月访问阿克拉，以讨论消耗臭氧层物质处置中心和其他项目活动的后勤问题。

<u>秘书处的评论</u>

102. 在该项目核准的 198,000 美元中，已经为国家和国际咨询项目拨付 21,000 美元。开发计划署通知秘书处，有关将要加工的消耗臭氧层物质的类型没有提供任何信息，因为对该项目来说还为时过早；然而，在加纳环境保护局储存的大部分消耗臭氧层物质和预计全环基金能效项目流出的消耗臭氧层物质是各类氟氯化碳，这种物质被确认为在项目得到核准后可以销毁的废物。

103. 开发计划署告知秘书处，该项目开始时有点慢，因为国际顾问在 2011 年访问加纳的时间必须与全环基金能效项目第一期讲习班的时间相吻合，以确保两个项目之间的协同增效模式安排到位。由于全环基金能效项目文件签署推迟，此项工作也有点延误。

<u>秘书处的建议</u>

104. 谨建议执行委员会：

(a) 注意到开发计划署提交的加纳的消耗臭氧层物质废物管理和处置试点示范项目的进度报告；以及

(b) 请开发计划署按照第 58/19（a）（三）号和第 64/50 号决定向执行委员会第六十九次会议提交关于加纳试点示范项目的进展情况和 获得的经验的报告。

六. 氟氯烃示范和投资项目

105. 开发计划署提交了关于下列氟氯烃项目的两份详细进度报告：

(a) 全球：关于在制造聚氨酯泡沫塑料系统时将甲缩醛用做发泡剂的评估报告（开发计划署）

(b) 全球：关于在制造聚氨酯泡沫塑料时使用碳氢化合物的费用选择的评估报告（开发计划署）

全球：在制造聚氨酯系统时将甲缩醛用做发泡剂。多边基金项目中应用情况的评估

背景

106. 开发计划署向第六十六次会议提交了关于在制造聚氨酯泡沫塑料系统时将甲缩醛用做发泡剂的技术报告：多边基金项目中应用情况的评估。本文件后附了完整的技术报告（附录二）。

107. 在第五十八次会议上，执行委员会核准了核查在制造聚氨酯泡沫塑料时将甲缩醛用做发泡剂的试点项目，但条件是，一旦该示范项目第一阶段和第二阶段完成，核查该技术所需的实验室设备将捐赠给非营利性研究机构（第 58/30 号决定）。

执行摘要

108. 开发计划署拟定了一些试点项目，以调查在聚氨酯泡沫塑料用途中安全使用甲缩醛替代 HCFC-141b 情况。Arinos Quimca 有限公司（巴西）评估了使用甲缩醛的系统的使用情况，目的是对照使用 HCFC-141b 的系统评估其绩效，以便确定此项技术用在多边基金项目中是否可行。

109. 为了确保全世界都能获得甲缩醛技术，开发计划署评估了供应方案。甲缩醛由比利时、中国、印度、大韩民国和大不列颠及北爱尔兰联合王国的制造商供应。尽管甲缩醛在若干种聚氨酯用途中申请了专利，但没有一项专利使得人们想过对其使用实行许可证制度。鉴于此，人们认为，这些专利中没有一种可以对在聚氨酯泡沫塑料使用甲缩醛索取有效而全面的知识产权。因此，可以得出以下结论，甲缩醛供应普遍，且免费用在泡沫塑料用途中。

110. 评估聚氨酯用途中的甲缩醛涉及以下问题：健康、安全和和环境因素；涉及其可加工性的问题（例如，稳定性、兼容性、航运和储存）；系统构成；从不同用途的试验中获得的物理性能概述；以及系统所在地和泡沫塑料企业采用这种技术的指示性转换成本。

111. 将 HCFC-141b 用做发泡剂的 16 种聚氨酯泡沫塑料用途得到了评估，因为它们有可能转用甲缩醛。为了评估开展了以下活动：购置必要的测试/原型制作设备；优化和鉴定所有 16 种原型设备拟订方案；拟定安全做法以达到系统所在地中和中小型企业含甲缩醛系统中的甲缩醛运输、储存和使用方面的国家和国际标准；以及通过讲习班传播获得的经验。下文表 5 归纳了评估综述。

表 5：为转用甲缩醛而评估泡沫塑料用途

用途	健康、安全、环境	可加工性	物理属性	评估
不绝缘泡沫塑料				
软质	+	+	+	+
鞋跟	+	+	+	+
结构性（硬质）	+	+	+	+
半软质	+	+	+	+
软质成型	+	+	+	+
超软块状	+	+	+	+
粘弹性成型	+	+	+	+
粘弹性块状	+	+	+	+

用途	健康、安全、环境	可加工性	物理属性	评估
包装用泡沫塑料	+	+	+	+
绝缘泡沫塑料				
制冷	+	+	+	+/-
热水器	+	+	+	+/-
卡车	+	+	+	+/-
块状、板状	+	+	+	+/-
喷射	+	+	+	+/-
塑料绝缘	+	+	+	+/-
聚异氰脲酸酯泡沫塑料	+	+	+	+/-

+ 好、- 差； +/- 尚可（根据情况而定）

112. 根据评估来看，在聚氨酯泡沫塑料用途中将甲缩醛用做发泡剂来替代 HCFC-141b 还是可行的。结果表明，甲缩醛更适合于不绝缘泡沫塑料而不是绝缘泡沫塑料。考虑到正在对优化的使用 HCFC-141b 的系统与最近开发的使用甲缩醛的系统进行比较，硬质（绝缘）泡沫塑料用途的研究结果导致绝缘值上升到 10 %。因此，如果要在这些用途中使用和进一步优化甲缩醛系统，应对各企业进行逐个评估。此外，采用甲缩醛技术必须满足以下条件：企业转产最好通过当地系统所在地进行；在项目编制期间核查化学兼容性，必须考虑与物质易燃性相关的影响。

113. 开发计划署制定了一般费用模板，以计算从 HCFC-141b 转向使用甲缩醛的泡沫塑料的增支成本。一个国家与另一个国家的资本费用（下表 6 所示）和化学成本可能相差悬殊，而且也受到规模经济因素的影响。

表 6：从 HCFC-141b 转向使用甲缩醛的泡沫塑料的相关资本费用

名称	指示性费用（美元）	评论
系统所在地		
混合池防爆	AA x 30,000	针对甲酸甲酯
注氮机	BB x 8,000	
甲缩醛蒸汽监测仪	2 x 2,500	监测工业卫生是否合格
喷射/套管安全一揽子措施	CC x 7,500	排气、接地
低/高压注入机安全一揽子措施	DD x 15,000	排气、接地
比重瓶（开孔/闭孔测试仪）	10,000	
便携式 K 系数测试仪	10,000	
折射计（测试化学纯度）	10,000	
供出租的小型注入机	EE x 15,000	
项目管理	FF 用户@ 1,000	
监测和技术转让	30,000	
应急费用	资本费用 10%	
客户（泡沫塑料企业）		
甲缩醛蒸汽监测仪	FF x 2,500	监测工业卫生是否合格*
喷射/套管改造一揽子措施	GG x 7,500	排气、接地
低/高压注入机改造一揽子措施	HH x 15,000	排气、接地
新注入机	II x 25,000	包括安全一揽子措施
试验、测试、培训,	KK 机 @ 3,000	同已核准项目
应急费用	资本费用 10%	

技术审查员的结论

114. 技术审查员得出结论，“第 5 条国家在聚氨酯泡沫塑料制造中使用甲缩醛以替换 HCFC-141b，似乎是一种可行的解决办法，达到了符合成本效益、消耗臭氧潜能值为零、全球变暖潜势低的替换技术的所有目的。泡沫塑料的最终性能堪比使用 HCFC-141b 的泡沫塑料”。技术审查员又建议，该报告应特别：界定测试结果参数以对实际作业环境对于泡沫塑料密度结果是否有预报价值提供指导；基于取得的结果对增支经营成本进行估算；继续对泡沫塑料性能，特别是尺度稳定性进行长期稳定性研究；将监测设备作为每个项目的组成部分以保证作业和人身安全。

秘书处的评论

115. 评价/评估甲缩醛的试点项目包括为传播项目成果 2011 年 12 月在巴西举办的讲习班，100 多名学员出席，其中包括以下实体的代表：巴西的 12 个系统所在地（8 家本国企业，即 Amino、Arinos、Ariston、M.Cassab、Polisystem、Polyurethane、Purcom 和 Utech 以及 4 家外国企业，即 Bayer、BASF、Dow 和 Huntsman）；来自巴西、牙买加及特立尼达和多巴哥的 13 家泡沫塑料制造商；5 个第 5 条国家（即哥伦比亚、巴拿马、巴拉圭、秘鲁和牙买加）；开发计划署、环境规划署和德国；3 个巴西行业协会；来自巴西、比利时和美利坚合众国的 8 家发泡剂制造商/经销商；6 家泡沫塑料注入设备制造商；以及 4 名泡沫塑料技术选择委员会成员。

116. 针对采用甲缩醛技术时需要对设备改造和/或新设备进行说明的要求，开发计划署解释说，使用甲缩醛时一般可以不改变基准设备。实际费用主要涉及泡沫塑料注入机的电气接地、安装甲缩醛感应器（替代办法是，系统供应商定期进行卫生检查）以及废气排放。只有在用户用手工制造泡沫塑料时，才需要新设备。

117. 在回答将甲缩醛用做泡沫塑料发泡剂时是否涉及专利和/或知识产权的问题时，开发计划署指出，甲缩醛的某些用途有多重专利。但是，综合起来看将甲缩醛作为聚氨酯泡沫塑料中的发泡剂没有专利，任何公司或其他实体都没有打算对标的用途的技术索取所有权。鉴于若干家大型化学品制造商在聚氨酯用途中都用过（并且仍在使用）甲缩醛，另外欧洲有近 30 家企业在使用，任何人索取此项技术并实施许可证制度都会非常难。因此，Lambiotte、Arinos 和开发计划署都认为，此项技术免费使用。

118. 在研究完秘书处和技术审查员提出的所有评论之后，开发计划署相应地修订了该示范项目的最后报告。

秘书处的建议

119. 谨建议执行委员会：

(a) 赞赏地注意到开发计划署提交的题为“在制造聚氨酯泡沫塑料系统时将甲缩醛用做发泡剂。多边基金项目中的应用情况评估”的报告；以及

(b) 在协助第 5 条国家编制在聚氨酯泡沫塑料用途中淘汰 HCFC-141b 的项目时，请双边和执行机构分享开发计划署关于甲缩醛的评估报告以及关于其他替代品的信息。

全球：在制造聚氨酯泡沫塑料时使用碳氢化合物的低成本选择。多边基金项目中的应用情况评估

背景

120.　开发计划署向第六十六次会议提交了关于在制造聚氨酯泡沫塑料时使用碳氢化合物的低成本选择：多边基金项目中的应用情况评估的技术报告。本文件（附录三）后附了完整的技术审查。

121.　在第五十八次会议上，执行委员会核准了鉴定/示范埃及在制造聚氨酯泡沫塑料时将碳氢化合物用做发泡剂的低成本选择（第 58/31 号决定）。

执行摘要

122.　使用碳氢化合物的低成本选择示范项目与其他试点项目的不同之处在于，前者侧重于优化现用的和广泛应用的技术成本和运行情况。高成本切实将碳氢化合物技术局限于大企业，并且间接导致小型企业和/或不太先进的企业普遍使用 HCFC-141b。由于低全球变暖潜势的影响，此类项目的资金门槛最近有所提高，设备费用也是如此。因此，中小企业只能重新使用对于环境不理想的氢氟碳化物，勉强运行水基系统，或希望新的技术评估将提供更加令人满意的选择。

123.　在最近 20 年里使用碳氢化合物技术没有发生实质性变化。它要求昂贵的预混和计量设备、防爆生产区和特别安全程序。另外，在许多国家，多年来系统配方没有改变，而改进添加剂、多元醇、共同混合选择和进一步优化，都有助于以相同或更低的成本取得更好的结果。

124.　示范项目分三个步骤执行，即：设备开发，通过标准采购程序选择一家合格的设备供应商提供的设备；由一家合格的系统所在地开发系统，包括在一家经得起检验的拥有适当能力的当地泡沫塑料制造商或系统所在地进行试用；以及报告，包括在向执行委员会提交最后报告之后为传播结果举办区域间讲习班。

125.　在执行项目期间，开发计划署确认了以下选择：在供应商一级降低预混成本，这将避免需要一台预混机加辅助设备（例如，储存罐、水管）；直接注入碳氢化合物，这也将排除预混系统之需；以及采用近期开发的碳氢化合物混合物，这将降低泡沫塑料密度。

126.　选中的设备是一台三舱高压注入机，能够处理全配方系统、直接注入易燃和不易燃发泡剂。在试用时，该设备在使用氟氯烃系统（基准）、预混系统和直接注入时运行良好。该注入机的重复率极高；可以接受三股混合（将来经过调整可以改善运行情况）；以及高效密封发泡剂，致使泡沫塑料密度降低。如下文表 7 所示，选中了 6 个不同系统。HCFC-141b 系统充当基准，而戊烷异构体反映了市场偏好。所有戊烷发泡系统被评估为全配方系统（含发泡剂）和部分混合系统（发泡剂添加为第三股）。

表 7：为测试挑选的泡沫塑料发泡系统

发泡剂	商用制冷	间断面板	热火器
HCFC-141b	系统 A	系统 C	系统 E
环戊烷	系统 B	系统 D	系统 F
普通戊烷	系统 B	系统 D	

127. 进行的测试得到的结果表明：

(a) 6 个月以内在标准条件下环戊烷系统的物理和化学稳定性得到证实。普通戊烷系统在 1 个月以后不再稳定；

(b) 就预混系统而言，因为需要非预混系统，预计可以节省成本约 100,000 美元；

(c) 尽管就直接注入而言没有节省设备成本，但密集型设计有助于布局和储存方面获得节省；

(d) 如果较低的自由密度可以“转化”为较低的应用密度，同 HCFC-141b 系统相比业务节余预计可达到 6%至 8%（直接注入可达到 10%）。然而，运输成本可能提高；

(e) 略高的 k 系数[1]（5%至 8%之间）和较低的反应速度表明，混合头碰撞式采样因出现第三股而受到影响。尽管用优化催化剂办法可以得到改善，但需要考试重新设施注入机的混合头。

128. 尽管所有技术说明被视为普遍有效，但费用说明只与埃及相关，对于其他区域/国家需要调整。尽管开发计划署确认了需要采取后续行动的若干领域（混合头效率、催化剂优化），但它认为，目前的结果很重要，为立即公布提供了依据。

技术审查员的结论

129. 技术审查员得出以下结论，此项研究核查了使用预混的碳氢化合物系统以及碳氢化合物直接计量的商用制冷、间断面板和热水器用途所需的硬质泡沫塑料产品令人可以接受的物理属性；研究还核查了 5 个月期限的环戊烷预混系统的稳定性；各项研究将继续核查至少 6 个月的使用寿命。研究还表明正戊烷系统由于混合产品不稳定不适合预混（相位分离）。研究表明使用三舱注入机旨在使预混和直接计量碳氢化合物系统之间的业务具有灵活性。

130. 研究没有充分核查新系统和设备的业务持续安全情况。应当进行额外研究，以产生数据，明确确定三组分混合业务达到了处理预混系统和直接计量的碳氢化合物时的安全要求，特别是在易燃性方面。应对预混多元醇系统运输和储存期间通风和监测的安全要求，包括预测费用提供进一步信息。分析转用这种预混/直接注入系统的预测费用应得到发展，以确定将从这一技术改良中受益的粗略估计用法水平。

秘书处的评论

131. 鉴定在制造聚氨酯泡沫塑料时使用碳氢化合物的低成本选择的试点项目包括为传播项目成果举办讲习班。在这方面，埃及举办了讲习班（2011 年 7 月 4 日至 5 日），学员如下：来自 5 个国家（埃及、阿拉伯联合酋长国、南非、巴西和意大利）的 11 个系统所在地；来自埃及的 19 家泡沫塑料制造企业；来自 5 个第 5 条国家（巴西、埃及、南非、土耳其和阿拉伯联合酋长国）的代表；来自开发计划署、环境规划署和工发组织的代表；

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[1] 材料单位厚度的热导率。

以及来自巴西和埃及的发泡剂批发商；3 家泡沫塑料注入设备制造商（多国）；以及 4 家主要国际聚氨酯化学品制造商的代表。在执行氟氯烃淘汰管理计划期间，包括在利益攸关方会议上以及访问泡沫塑料公司和系统所在地时向一些国家（巴西、尼日利亚、墨西哥）传播了试点项目结果。其中大多数国家表现出了兴趣并提出了询问。

132. 秘书处要求就使用碳氢化合物系统在企业一级将产生的潜在增支费用做出进一步解释。在答复这一要求时，开发计划署解释说，碳氢化合物预混多元醇属于危险货物并且被归类为易燃品。因此，储存多元醇的工厂应当适合储存易燃货物。鉴于企业之前使用过预混多元醇，总体空间要求与原来相同，泡沫塑料业务与使用纯碳氢化合物的业务相似，因此，与安全相关的设备和系统应当安排到位。主要差别在于，实地不需要预混，因而下游用户不必知道系统构成。化学成份（纯碳氢化合物）少了一个，业务也少了一项（预混器和辅助设备），企业一级的基础设施简化。

133. 鉴于技术审查员提出需要提供关于安全和费用相关问题的补充信息，开发计划署将进行额外的相关调查，重点放在为两种办法（直接注入、预混系统）专门设计安全概念；从预混多元醇获得的自由上升密度降低的明显事实和直接注入可能导致产品密度降低（可以接受）；混合头优化；将直接注入法推广到符合成本效益的改型模式以及基于本报告的成本计算概念。这些后续调查的结果将在提交给第六十七次会议的补充报告中列示。

<u>秘书处的建议</u>

134. 谨建议执行委员会：

(a) 赞赏地注意到开发计划署提交的题为“在制造聚氨酯泡沫塑料时使用碳氢化合物的低成本选择：多边基金项目中的应用情况评估”的报告；

(b) 请开发计划署最后确定关于安全相关问题、密度和设备优化的补充调查，根据预混碳氢化合物多元醇设计成本计算概念，并向第六十七次会议提交一份补充报告；以及

(c) 在协助第 5 条国家编制聚氨酯泡沫塑料用途中淘汰 HCFC-141b 的项目时，请双边和执行机构分享开发计划署关于在制造聚氨酯泡沫塑料时使用碳氢化合物的低成本选择的评估报告，以及关于其他替代办法的信息。

Annex I

DETAILED WORK PLAN AND BUDGET ESTIMATES FOR NCPP ACTIVITIES, CY 2012 until April 2013

Programme Element	Specific Activities (provide details)	Target	Budget estimate (for each activity within each programme element) US$	Period of implementation (include month and year)	Secretariat's proposal
1.Project Management	1.1 PMU Staff costs	8	88,550	Jan 2012-April 2013	88,550
	1.2 Maintenance and Other Operating Expenses (supplies, communications, repairs and maintenance of equipment, gasoline and other lubricants, miscellaneous and contingency)		47,619	Jan 2012-April 2013	20,000
	1.3 Attendance to Annual consultations/meetings (local/international)	4	58,000	Jan 2012-April 2013	20,000
	1.4 **Training/Seminars/Workshops (local and international)**				10,000
	1.4.1 Attendance to financial and administrative workshop to harmonize the policies of UNEP and the GoP	1	8,200	June 2012	
	1.4.2 Attendance to technical training to ensure the compatibility of Philippine system with China web-based system in tracking the stock of CFCs in the global market	1	19,048	3rd Quarter of 2012	
	1.4.3 Follow-up training of partner agencies and regional offices on database management and maintenance	4	28,571	3rd Quarter of 2012	
	1.4.4 Regional forum on the updates of the NCPP Project Implementation and other NCPP implementation requirements	2	28,572	June 2012-April 2013	
	1.5 **Turn-over of training equipment to Training Institutes**	150 sets			5,000
	1.5.1 Conduct meetings with TESDA on the findings of the assessment on the training equipment conducted by NCPP-PMU	12	286	Jan -June 2012	
	1.5.2 Conduct physical verification of training equipment nationwide	16 regions			
	1.5.3 Conduct of final inventory of project fixed assets and preparation of turn-over documents and/or deed of donations to EMB Regional Office and partner agencies		11,905		
	1.5.4 Preparation of documentary requirements and distribution of deed of donations	150 Training Institutions & 16 EMB Regional Offices			
	1.7 **Preparation of Project Completion Report of overall implementation of the NCPP (for the period 2012-2014)**				
	1.7.1 Hiring of Individual Consultant for the preparation of PCR	1	4,762	January-April 2013	
	1.7.2 Conduct of annual financial audit	2	4,762	2012-2013	
	1.7.3 Preparation/Finalization of reports (closing of books, meetings with partner agencies, TWG, etc.)	2	1,429	January-April 2013	
Sub-total			**194,169**		**143,550**

Programme Element	Specific Activities (provide details)	Target	Budget estimate (for each activity within each programme element) US$	Period of implementation (include month and year)	Secretariat's proposal
2.Prevention of additional supply of ODSs/HCFCs	2.1 Hiring of auditing firm to conduct Verification Audits for CFCs and HCFCs 2.1.1 CY 2009&2010 (HCFCs) 2.1.2 CY 2011-2013 (CFCs and HCFCs)	2 4	47,619	2nd Quarter of 2012 Every 1st Quarter of 2012 and 2013	30,000
	2.2 Hiring of IT firm to develop a web-based CFC/HCFC import and export monitoring system	1	23,810	4th quarter of 2012	10,000
	2.3.1 Conduct of BOC Customs Officers Training nationwide on the developed web-based CFC/HCFC imports and exports monitoring system 2.3.2 Conduct technical training for BOC inspectors on skills in the identification and close montoring of HCFC and equipment using HCFC	4	47,619	1st quarter of 2013	20,000
	2.4 BoC enforcement of approved regulatory and policy measures for HCFC reduction and eventual phase-out 2.4.1 Provide regulatory support to BoC on the implementation on the revised CCO	1	7,142	January 2012-April 2013	
	2.5 Monitoring of grant recipients under type 1 subprojects (conversions) in compliance with CFC/HCFC regulations 2.5.1 Conduct of compliance monitoring of completed investment projects	5 (Phase 2)	4,762	2012-April 2013	
	2.5.2 Provide regulatory support to FDA on the conduct of market monitoring of compliance of pharmaceutical industry, medical practitioners, and MDI users on the phase out of CFC-containing MDIs.	16	4,762	2012-April 2013	5,000
	2.6 Implementation of the amended IRR of PD 1572 specifically on the accreditation of service shops 2.6.1 Provide regulatory support to DTI and LGUs on the service shops' full compliance to the accreditation requirements 2.6.2 Monitoring of service shops nationwide in coordination with DTI and BPLO	16 DTIs 2521	7,143 28,571	2012-April 2013	

Programme Element	Specific Activities (provide details)	Target	Budget estimate (for each activity within each programme element) US$	Period of implementation (include month and year)	Secretariat's proposal
	2.7 Conduct of compliance monitoring on the registration of ODS Handlers, dealers and resellers nationwide	16	7,937	2012-April 2013	
	2.8 Development and publication of Philippine National Standards for refrigerant cylinders and other HCFC appliances	1	7,143	1st quarter of 2013	
Sub-total			**86,509**		**65,000**
3. Elimination of CFC demand in the country	3.1 **Updating of the Code of Practice Manual on Refrigeration and Airconditioning to include other new chemicals & technologies**				15,000
	3.1.1 Hiring of a Technical Expert/Consultant	1	7,143	2nd Quarter of 2012	
	3.1.2 Coordination meetings with core group consist of 5 technical groups/associations that would prepare the draft COP	1	4,286		
	3.1.3 Conduct of Regional consultations nationwide on the updated Code of Practice	3	21,426	3rd and 4th Quarter of 2012	
	3.2 Assessment of Service Shop Voucher Grantees				5,000
	3.2.1 Hiring of Regional Coordinators	10	12,753	3rd Quarter of 2012	
	3.2.2 Conduct of actual survey	1,339	25,505		
	3.2.3 Hiring of M& E Consultant for the assessment of Training Institutes and Service Shop grantees (85% audit)	1	3,524		
	3.2.4 Regional consultation on the draft assessment report	4	21,423	4th Quarter of 2012	
	3.2.5 Finalization of assessment report	1			
	3.3 Support to regional monitoring and validation on the findings of the technical and system audit in compliance to the terms and conditions of the voucher system	16 Regions 2521 service shops	57,143	1st quarter of 2013	40,000
	3. 4 Conduct of re-training of trainers of TESDA and TESDA accredited institutions nationwide particularly on the implementation of the 3RS and the inclusion of new chemicals including HCFCs and other technologies in the updated CoP.	300 TESDA Trainers	35,714	3rd and 4th Quarter of 2012	30,000
	3.5 Support to TESDA on the conduct of regional assessment and certification of remaining service technicians nationwide 3.5.1 Training supplies and materials 3.5.2 Travelling expenses 3.5.3 Coordination meetings with TESDA assessors and focal persons	980 service technicians	16,333	1st quarter of 2013	

Programme Element	Specific Activities (provide details)	Target	Budget estimate (for each activity within each programme element) US$	Period of implementation (include month and year)	Secretariat's proposal
	3.6 Regulatory support to LTO in compliance to the JAO 03 series of 2006: Enforcement of Regulation on the Implementation of the NCPP on Motor Vehicles under the Revised Chemical Control Order for ODS: 3.6.1 Conduct coordination meetings with LTO on the preparation of assessment report on the compliance of motor vehicles to refrigerant type 3.6.2 Provision of refrigerant identifiers to LTO district offices (only in 6 key areas nationwide) to fully implement the banning of motor vehicles equipped with CFC MAC starting January 2012 3.6.3 Conduct of MAC random roadside inspection by a composite team on a quarterly basis	10 108 80	1,190 205,714 9,524	2nd Quarter of 2012 2012-April 2013	80,000
Sub-total					**170,000**
4. Management of unwanted ODS	4.1 Collection, transport and storage of recovered refrigerants from service shop grantees and chiller owners nationwide including confiscated refrigerants 4.1.1 Conduct coordination meetings with DELSA on the CTS scheme to cover other regions 4.1.2 Hauling of collected/confiscated refrigerants (from regional key areas to central CTS facility)	16 regions	72,857	2012-April 2013	30,000
	4.2 **Procurement of additional Equipment for the collection, transport and storage of recovered refrigerants from service shops, chiller owners, etc.** 1. 10 units of 1 tonne tank/cylinder 2. 4 units Recovery Machine 3. 1 unit Transfer Pump 4. 20 units (100 KG Cylinder) 5. 1 unit Moisture meter for quality assurance for recoverable contaminated refrigerants		79,546	2nd Quarter of 2012	
Sub-total			**152,403**		**30,000**

Programme Element	Specific Activities (provide details)	Target	Budget estimate (for each activity within each programme element) US$	Period of implementation (include month and year)	Secretariat's proposal
5. IEC and Public Awareness	5.1 Conduct of advocacy and communication skills enhancement training in Luzon, Visayas and Mindanao	4	26,190	4th Quarter of 2012	20,000
	5.2 Conduct of orientation seminars among BPLO of LGUs and DTI on accreditation requirements	300	30,357	3rd Quarter of 2012	
	5.3 **Development and production of IEC materials** - Amended CCO for ODS - Revised Code of Practice - Updated NCPP Primer including HCFC - Brochures and leaflets - Tarpaulins/Posters - Newsletters - Web Pages that highlight service shop benificiaries - E-learning training modules - Social Networking - Video Documentary		45,456	2012-April 2013	
	5.4 Production and airing of broadcast media on ozone layer depletion, NCPP major achievements, ban of CFCs in RAC/MAC sector and reduction as well as banning of HCFCs		90,476	2012-April 2013	
	5.5 Ad hoc promotional activities during Ozone Month and Earth Day Celebrations.	3	21,429	2012 -April 2013	
Sub-total			**20,000**		**20,000**
GRAND TOTAL			**453,081**		**428,550**

ATTACHMENTS

Attachment I	Progress Report on the Implementation of the Executive Committee Decision 64/20 on the Institutional Strengthening project of DPR Korea submitted by UNEP.
Attachment II	“Methylal as blowing agent in the manufacture of polyurethane foam systems. An assessment for the application in MLF projects” submitted by UNDP.
Attachment III	“Low cost options for the use of hydrocarbons in the manufacture of polyurethane foams: An assessment for the application in MLF projects” submitted by UNDP.

Progress Report on the Implementation of the Executive Committee Decision 64/20 on the Institutional Strengthening project of DPR Korea

A. Background:

The 64th meeting of Executive Committee (25-29 July 2011) discussed the submission of DPR Korea's Institutional Strengthening project (ISP) renewal. The following is the extract of the final report of that meeting concerning this issue:

Paragraph 86. Concern was expressed about the lack of transparency and difficulties in monitoring the exact use of any institutional strengthening funding in the Democratic People's Republic of Korea.

Paragraph 87. The Executive Committee decided:

(a) To defer consideration of the request for phase VI of the institutional strengthening project for the Democratic People's Republic of Korea to its 66th meeting; and
(b) To request the Secretariat and UNEP, as implementing agency, to propose alternative methods of disbursement, organizational structures and monitoring procedures to the Executive Committee by its 66th meeting.

(Decision 64/20)

On the margins of the 64th Executive Committee meeting, UNEP discussed with relevant Committee members that are interested in this topic, to provide additional information. During that side meeting, the following specific issues were raised clarifying the intent of the Decision 64/20:

- The salary level of the Ozone Officer and the modalities of salary payment under the ISP: It was noted that the cost of the salary is high and not in line with local salaries and the payment to the Ozone Officer through the Government needs more transparency. As an alternative, it was suggested if it was possible for UNDP Pyongyang to pay the Ozone Officer with a reduced salary level?
- The UNEP delegation was provided with a document that had details about UNDP's new Internal Control Framework for implementation of projects in DPR Korea. UNEP was asked to explore to which extent the ISP project could be implemented in light of such a framework.
- Possibility for the Ozone Officer to be housed in UNDP's Pyongyang office.

Following the Executive Committee decision and the above discussions, UNEP's Compliance Assistance Programme (CAP) informed DPR Korea's National Ozone Unit (NOU) about the Executive Committee Decision 64/20, and sent a formal letter to the UNDP Representative in Pyongyang through the Director of UNEP's Regional Office for Asia and the Pacific (ROAP) to initiate the consultation. It later agreed that the consultation would be conducted in Pyongyang during a joint UNIDO/UNEP mission for the country's HPMP preparation during 28 November to 1 December 2011.

UNEP prepared a draft report based on consultations in Pyongyang and circulated it to the Multilateral Fund Secretariat for review and comments. UNEP has also been keeping relevant Executive Committee delegations informed of these consultations. Based on comments/input received, UNEP finalized the report for the consideration of the Executive Committee.

The following three parts describe the current implementation modality of the IS project in DPR Korea, the consultation process in Pyongyang and the proposed alternative methods for disbursement, organizational structure and monitoring procedures as requested by the Decision 64/20 of the Executive Committee. At the end of the report, recommendations are proposed for the consideration of the Executive Committee at its 66th meeting.

B. Current methods of disbursement, organizational structures and monitoring procedures for the implementation of the Institutional Strengthening Project

Disbursement

Under the current financial system, UNEP has been transferring the approved fund under the Institutional Strengthening Project to DPR Korea through the Small Scale Fund Agreement (SSFA). Following the signature of SSFA between DPR Korea and UNEP with the agreed work plan, the first payment would be made as cash advance to support the NOU to conduct the planned activities. Upon receipt of a satisfactory interim progress report and financial reports and confirming that 80% of first payment has been spent, UNEP would proceed with making the second payment. This modality is applying to all ISPs that UNEP is implementing as the implementing agency.

The cash advance and the later reimbursement will be diverted to the National Ozone Unit, National Coordination Committee for Environment (NCCE) through UNDP Pyongyang in local currency.

Organizational Structure

The National Ozone Unit (NOU) is one of the core organs under the National Coordinating Committee for Environment (NCCE), which is chaired by the Vice Minister of the Ministry of Foreign Affairs. NOU is administrated by NCCE and supported by project officers and coordinators overseeing the activities relating to Montreal Protocol. All staff working in NOU is appointed by the Government of DPR Korea.

Monitoring procedure

As specified in SSFA, the NOU needs to submit regular progress report on the implementation of the agreed work plan as well interim and final financial report for UNEP's review. The NOU would also share the final products such as the newsletters, poster etc that produced under the ISP with UNEP. UNEP maintains regular contact with NOU through UNDP Pyongyang on any queries, and/or clarification; Further UNEP takes supervision and inspection mission from time to time to visit Pyongyang, in combining with the implementation of other approved activities under Multilateral Fund. UNEP also have participated in some of activities organized by the NOU such as Ozone Day Celebration in Pyongyang.

C. Consultation Process in Pyongyang during 28 November-1 December 2011

Meeting with National Coordination Committee for Environment (NCCE)/NOU

UNEP and the NCCE of DPR Korea first jointly reviewed the Decision 64/20, and identified possible alternatives that the NOU could consider. The following issues were highlighted during the discussion:

General Issues:

- The NOU first raised concerns about the impact of the delayed approval of ISP for the country’s compliance, and requested UNEP to convey a similar message as recorded in the final report of the Joint Meeting of the South Asia-South East Asia Regional Network of ODS Officers in Pokhara during 17-19 October 2011 on this matter, i.e.“ Network countries felt that the IS funding is essential for successful implementation of the Montreal Protocol and Executive Committee should be informed of countries concerns of difficulties that may face if any disruption or delay in funding of IS projects”.
- The NOU further stated that it would cooperate with UNEP and the Multilateral Fund Secretariat to explore possible alternatives as requested by the Executive Committee, even though it was not convinced that it should be singled out for such a treatment.
- The possibility to transfer the ISP to UNDP was discussed. However the NOU preferred that UNEP continues implementing the ISP considering the long term cooperation with UNEP for more than 20 years, and national stakeholders’ familiarity with UNEP’s reporting requirements and procedures.

Disbursement

- The option to stop advance payment under the current system was discussed. This means that following the signing of the SSFA, the NOU would need to organize the planned activities by using funding from other internal resources, and upon the submission of the progress report, the financial report and the receipts, UNEP would reimburse the cost accordingly through UNDP Pyongyang. The NOU warned that without advance payments under the ISP, the planned activities may not be organized as originally planned, as it will depend on the availability of the funding in the other departments of the Ministry. Therefore, it might delay the project implementation. The NOU advised it would be more efficient to continue the current advance payment system, but strengthen the management and monitoring on the use of the advance payment.

Organizational Structure

- Concerning the NOU’s staff recruitment, the NOU was flexible for the local people to be contracted by UN organization following the established procedures of UNDP, and make payments to those people directly.

Monitoring procedure

- Regarding the monitoring of the activities under the ISP, the NOU agreed to coordinate with UNEP more closely, to enable UNEP staffs who are visiting DPR Korea for other activities to participate in these activities. The NOU further agreed to provide UNEP with a separate report for each event they organized under the ISP within two weeks of completing the activity.

Meeting with UNDP, Pyongyang Office

UNDP Pyongyang has been extremely cooperative, and further showed its support to the work UNEP is carrying out in DPRK and expressed its readiness to extend its support if the working environment permits.

UNDP in DPRK has a special Internal Control Framework and signed a MoU with the DPR Korea Government specifying those special operating arrangements under finances, banking, human resources, procurement and reporting.

UNDP is directly implementing its projects under the Direct Implementation Modality (DIM). For an example, no advance payments is allowed under DIM, and UNDP should implement all the activities and make payments directly to the vendors for the goods and services and pay in local currency to their local bank accounts of the vendors. UNDP national personnel should be hired under UNDP contracts and are considered UNDP staff. The procurement of goods and services follow the same strict regime and controls, UNDP verify each requisition for goods and services against the lists of Items Prohibited for Export to and Import from DPRK pursuant to UNSCR 1718 including checking the items against the category "double use items" and accordingly UNDP requests vendors to provide export licenses for goods containing at least 10% of US or Japanese made components or technology.

UNEP can completely hand over the project to UNDP Pyongyang to be implemented under UNDP DIM. This means that the project will be completely managed under UNDP rules and regulations, and the complete budget should be transferred to UNDP to implement the project and not only part of it, this includes managing the staff and resources, activities and payments. UNDP for that will charge its fixed General Administration fee of 7% as well as the Implementation Support Services for DIM projects, which should be added to the total budget of the project. It concluded that it would be more cost effective if the ISP could be directly implemented by UNDP as the implementing agency.

However, it also recognized that the country's preference of continuing with UNEP should be respected. In addition, if the ISP is to be transferred, the financial implications to the Multilateral Fund due to the charging structure for programme support cost (PSC) for the ISP, also needs to be considered. UNEP is open to any alternatives, including transfer of the ISP to other implementing agency such as UNDP which will need consultations with UNDP Montreal Protocol Unit.

It was noted that as per the salary level determined by International Civil Service Commission (ICSC), the current salary level of the NOU staff under the ISP is reasonable. Currently, the proposed salary level for the 3 staff of the NOU is about USD 520/month per person on an average. For comparison, the salary level of local professional working on other projects for UNDP is about USD 900-1,000/month as per the established salary level by ICSC. If UNEP needs to hire the local staff directly, as per UNDP procedure the salary level would need to be increased, which will mean additional burden on MLF and will not be consistent with the Excom decisions on funding levels for ISPs.

For the housing the NOU staff, UNDP Pyongyang informed UNEP that it has space constraints currently and in fact one of its project office is located outside of UNDP component in Pyongyang as well. Therefore, to house 3 staff of NOU in UNDP Pyongyang office would be difficult. Also it recognized due to the nature of the work of NOU, it might not be efficient for NOU to be located in UNDP compound as well.

UNDP Pyongyang also advised UNEP to contact other agencies that are operating in DPR Korea to understand their execution modalities. Later, United Nations Children's Fund (UNICEF) confirmed that "UNICEF has a full fledged office here in Pyongyang, DPR Korea and manages its activities like any other country office does".

UNEP internal consultation

Concerning the direct contract the local people who are working for NOU, UNEP ROAP consulted UN Economic and Social Commission for Asia and the Pacific (ESCAP) that is providing administrative service to UNEP ROAP. It was advised that ESCAP would not be able to contract the Ozone Officer without daily supervision in Pyongyang. Therefore, UNEP would not be a position to recruit the local people.

It was agreed that the following alternatives could be submitted to the Executive Committee for consideration after further consultation with the Multilateral Fund Secretariat.

D. Proposed alternative methods of disbursement, organizational structures and monitoring procedures

Fund disbursement approach under the ISP:

Activities:

All activities under ISP would be undertaken locally, such as public awareness events, UNEP and NCCE would sign a financial agreement (SSFA) to clearly define all activities and the respective costs. UNEP, as per the financial agreement, would make advance payments in Korean Won through UNDP Pyongyang after a detailed workplan for the year has been submitted listing the activities that will be conducted. However, the advance payment would not be spent for any of these activities unless the NOU submits a separate further detailed Terms of Reference (TOR) for each of the planned activities at least one month before the activity, for endorsement by UNEP. It was also agreed that within two weeks following the completion of the activity, the NOU would submit to UNEP a detailed report of the activity undertaken against the endorsed TOR with expenditure reports as well as original receipts for UNEP’s review and monitoring. For any activities that are organized without UNEP’s pre-endorsement, UNEP would not agree to cover the cost from the advance payment under the ISP.

Organization Structure:

The NOU staff would be recruited by the Government, and would be physically located in Ministry of Environment and Land Protection. UNEP, UNIDO and their consultants could easily visit the NOU office during their missions, and the NOU staff would be invited to the meetings of the Regional Networks of Ozone Officers, as well as other relevant meeting concerning the implementation of the Montreal Protocol.

Monitoring Procedures:

As agreed with NCCE, in addition to the semi-annual progress report that is required for any country as per UNEP procedures, the NOU of DPR Korea would conduct each planned activity as per pre-endorsed TOR following the above mentioned procedure and submit activity report within two weeks of completion of the activity. In addition, UNEP would coordinate with the NOU on the timing of the organization of any activity to maximize UNEP staff’s physical participation in ISP activities. UNEP has other projects with DRP Korea beyond those of the Multilateral Fund, and there are visits by UNEP ROAP (i.e. non-CAP) staff to Pyongyang frequently which will also be utilized for such monitoring. UNEP CAP would also try its best to organize its visits twice a year to conduct review and supervision work.

The NCCE also agrees that UNEP would have unhindered access to project sites, as necessary for the implementation, monitoring and oversight of its programme.

Recommendation:

The Executive Committee might like to consider the following in light of the consultation and discussion as reported above:

- Take note of the consultations made by UNEP and the Multilateral Fund Secretariat and proposed alternatives;
- To approve the ISP renewal for DPR Korea, and request UNEP to implement the ISP as per the proposed alternatives in Section D above;
- To request UNEP to report back the implementation status of the proposed alternative when it submit the renewal of the ISP for DPR Korea to the further coming meeting of the Executive Committee.

or

- Take note of the consultations made by UNEP and the Multilateral Fund Secretariat and the proposed alternatives;
- To request other IAs who are interested in the implementation of the IS project for DPR Korea to further consultation with the Government of DPR Korea following Decision 64/20 with alternative methods of disbursement, organizational structures and monitoring procedures to the Executive Committee by its 68th meeting.

METHYLAL AS BLOWING AGENT IN THE MANUFACTURE OF POLYURETHANE FOAM SYSTEMS

AN ASSESSMENT FOR APPLICATION IN MLF PROJECTS

MARCH 2012
-FINAL DRAFT-

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EXECUTIVE SUMMARY

Common technologies for replacing HCFC-141b include water/isocyanate, hydrocarbons and HFCs. Water may have limitations in thermal insulation applications; HFCs usually have high GWP values and hydrocarbons high in investment costs. There is therefore a need to assess other potential alternatives and, therefore, to investigate emerging/emerged technologies on their properties, costs, availability, sustainability and environmental performance. Decision 55/43 by the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol ("MLF") reflects this by promoting pilot projects aimed at validating technologies in a developing country ("A5") context.

This particular pilot project—the use of methylal ("ML")—has been designed around Arinos Quimica Ltda ("Arinos") in Sao Paulo, Brazil, a large independent system house producing PU systems that cover most PU applications, with input from Lambiotte & Cie/Belgium, a major supplier of methylal and a proponent for its use in PU foams and assistance from Dow-Brazil for product testing. To assure that methylal technology would be available world-wide, UNDP has first assessed the supply scenario. It has found that methylal is offered by manufacturers in Belgium, England, India, Korea and China. While methylal has been patented for a multitude of narrow PU applications, none of these patents cover broad use and/or have resulted in attempts to license its use and Lambiotte is of the understanding that none of these patents can claim effective and comprehensive intellectual rights on the use of methylal in PU foams. Therefore it can be concluded that methylal is commonly available and free to use in foam applications. The assessment addresses in sequence

- Health, safety and environmental considerations,
- Processability, including stability, compatibility shipping and storage
- System composition information
- Overview of physical properties obtained from trials for different applications
- Indicative conversion costs
- Conclusions and recommendations

Sixteen different PU foam applications have been identified that use currently HCFC-141b and these have been evaluated on the potential use of methylal as blowing agent with HCFC-141b as baseline technology to compare with. The different activities included:

- Acquisition of the necessary testing/prototyping equipment;
- Optimization and validation of all 16 formulations on prototyping equipment;
- Development of safe practices meeting national and international standards for the transportation, storage and use of methylal in system houses and of methylal-containing systems at SMEs;
- Dissemination of the experience gained through a workshop.

It is emphasized that this assessment serves a very practical purpose which is to

Determine the extent to which methylal can be satisfactorily used in MLF-funded HCFC phase-out projects and, in this way, avoid unexpected setbacks in project implementations

This does not include an exhaustive investigation into the way the technology works. It does, however, include back-to-back testing with the technology it replaces as well as a review of existing data, specifically on health, safety and environment. Some limited industrial hygienic testing has been conducted as well.

Implementation started with a review of the 18 originally earmarked applications to assess the possibility to combine applications based on same or very similar formulations, determination of the assessment parameters and critical issues for acceptability. The applications template was then functionally rearranged and reduced as follows:

Foam type	Application		Critical Properties	Developed and tested
Non Insulating Foams	Integral skin foams	Flexible	Friability, surface	√
		Shoe soles	Surface	√
		Structural (rigid)	Surface	√
		Semi-flexible	Surface	√
	Flexible foams	Flexible molded	Appearance, touch	√
		Hyper-soft block	Appearance, touch	√
		Viscoelastic molded	Slow mechanical recovery	√
		Viscoelastic block	Slow mechanical recovery	√
	Semi-rigid foams	Packaging foam	Shock absorption	√
Insulating foams	Rigid PU/PIR foams	Refrigeration	Insulation, adhesion, dimensional stability, (lack of) water permeability	√
		Water heaters		
		Trucks		
		Blocks, Panels		
		Spray		
		Thermoware		
		PIR Blocks		

Acceptability, for the purpose of this project, is defined as:

- Determining the safe use of the technology based on health, safety and environmental (HSE) data;
- Determining the applicability of the technology based on processability and relevant physical properties;
- Collecting complementary information, views from enterprises that have tested ML formulations.

Based on the information presented in this report and its attachments It can be concluded that methylal:

- Does not create incremental health concerns;
- While on downstream level mitigated through preblending, still requires safety measures as outlined;
- Does not pose an environmental hazard;
- Shipments and storage in its pure form must comply with its flammability status (GHS);
- In fully formulated systems <2% methylal (polyols) or <2% methylal (isocyanates) requires no special safety considerations. Systems containing 2-5 php need individual consideration and above that level, compliance with GHS category 2 or 3 is required. Local regulations are also to be complied with;
- In fully formulated systems for all applications are stable.
- In blends are not corrosive;
- In blends with polyols and/or additives do not pose compatibility issues. However, it is recommended that when designing conversion projects, the compatibility of baseline polyols will be carefully checked and the impact on flammability characteristics determined;
- Has in systems a shelf life of at least 6 months under standardized conditions;
- In non-insulation foams, regardless of application ML matches, in a narrow margin, HCFC-141b foams. With more optimization, even better results can be expected;
- In thermal insulation foams match HCFC-141b foams within an acceptable range (+/- 5%) in stability and density but carry a penalty in insulation value.

Also:

- No data on long-term performance are as of yet available;
- Customers selected for performance trials—one per application—all expressed their agreement with the performance of methylal-based PU systems.
- Conversion cost estimates show relatively low capital and operating costs:

Incremental Capital Costs

ENTITY	ACTION	CALCULATION	Comment
System House	Explosion proofing of blending tanks	AA x 30,000	As for methyl formate
System House	Nitrogen dispenser	BB x 8,000	
System house	ML vapor monitors	2 x 2,500	To monitor IH compliance
System House	Spray/PIP safety package	CC x 7,500	Exhaust, grounding
System House	LPD/HPD safety package	DD x 15,000	Exhaust, grounding
System House	Pycnometer (closed cell tester)	10,000	As FSPOP project template
System House	Portable K-factor tester	10,000	
System House	Refractometer (test chemical purity)	10,000	
System House	Small rent-out dispenser	EE x 25,000	
System House	Project Management	FF clients @ 1,000	
System House	Monitoring & technology transfer	30,000	
System House	Contingencies	10% of capital costs	
Customers	ML vapor monitor	FF x 2,500	To monitor IH compliance*
Customers	Spray/PIP retrofit packages	GG x 7,500	Exhaust, grounding
Customers	LPD/HPD retrofit package	HH x 15,000	Exhaust, grounding
Customers	New Dispensers	II x 35,000	Include safety packages
Customers	Trials, testing, training,	KK machines @ 3,000	As in approved projects
Customers	Contingencies	10% of capital costs	

Incremental Operating Costs (based on 10/2011 pricing)

CHEMICAL	PRICE (US$/kg)	BASELINE		Expert A		Expert B		Expert C		Cost Base	
		%	Cost	%	Cost	%	Cost	%	Cost	%	Cost
Polyol	3.20	38	1.22	40	1.28	40	1.28	42	1.34	42	1.34
Isocyanate	3,00	50	1.50	52	1.56	54	1.62	50	1.50	50	1.50
HCFC-141b	2.40	12	0.29	--	--	--	--	--	--	--	--
Methylal	4.00	--	--	8	0.32	6	0.24	8	0.32	8	0.32
Cost			3.01		3.16		3.14		3.16		3.16
Difference			**Base**		**0.15**		**0.13**		**0.15**		**0.15**

It should be pointed out that these costs can differ significantly over time, from country to country and based on comparative size.

Following is a consolidated overview of the findings of this report:

Foam Type	Application	Assessment				
		HSE	Processing	Flamma/ Bility*	Physical Properties	Results
Non insulation foams	Flexible	+	+	+	+	+
	Shoe soles	+	+	+	+	+
	Structural (rigid)	+	+	+	+	+
	Semi-flexible	+	+	+	+	+
	Flexible molded	+	+	+	+	+
	Hyper-soft block	+	+	+	+	+
	Viscoelastic molded	+	+	+	+	+
	Viscoelastic block	+	+	+	+	+
	Packaging foam	+	+	+	+	+
Insulation Foams	Refrigeration	+	+	+/-	+/-	+/-
	Water heaters	+	+	+/-	+/-	+/-
	Trucks	+	+	+/-	+/-	+/-
	Blocks, Panels	+	+	+/-	+/-	+/-
	Spray	+	+	+/-	+/-	+/-
	Thermoware	+	+	+/-	+/-	+/-
	PIR	+	+	+/-	+/-	+/-

HSE + Good (compliance with international standards)
Processing: + Good (agreement as per customer who carried out the qualifying trials);
Flammability: + Non flammable (Cleveland closed cup test; as per formulations in attachment VII)
+/- May be flammable (Cleveland closed cup test)
Phys. Properties: + Good (agreement as per customer who carried out the qualifying trials based on +/- 5% range of results)
+/- Fair (acceptance is subject to company´s willingness to adopt a somewhat less favorable insulation value).
Note*: Source Lambiotte / Arinos

Note on flammability tests – the tests typically used to determine flammability (open and closed cup tests) are typically designed for transportation purposes and do not reflect very well danger in the workplace. For that reason, the EU has for processing purposes different tests, emphasizing the sustainability of a fire from emissions. Lambiotte reported that ML-based systems with less that 8 php ML do pass such tests. UNDP intends to commission a review of the flammability of all HCFC-141b replacements to be conducted by a recognized flammability expert.

Based on this assessment, the use of methylal as an alternative blowing agent to replace HCFC-141b in PU foam applications in MLF projects is considered feasible. The results indicate, however, that it is better suited for non-insulation foams than for insulation foams. Taking into consideration that the baseline is the comparison between optimized HCFC-141b based systems and recently developed methylal-based systems, the results for rigid (insulation) foams applications carries a penalty in insulation value of up to 10 %. However, there is room for further optimization such as cell size reduction and choice of surfactants and catalysts. This should be individually evaluated by system houses and other suppliers.

The adoption of methylal should be subject to the following conditions:

1. Projects should preferably be implemented through local system houses;
2. Project designers should ensure that:
   a. Chemical compatibility is verified,
   b. Implications related to the flammable character of the substance are addressed as recommended.

This pilot project included a workshop to disseminate the results of the project. This workshop was held in Brazil, at 6th and 7th of December 2011, with the 108 attending from 12 system houses from Brazil; 13 foam manufacturers from Brazil, Jamaica and Trinidad/Tobago; other representatives from five Article 5 countries (*Colombia, Panamá, Paraguay, Peru and Jamaica*); representatives from UNDP, UNEP and GIZ; three Brazilian industry associations (*Abripur, Abiquim and Abrava*), eight blowing agent manufacturers/distributors (*from Brazil, Belgium and United States*) and six foam injection equipment manufacturers. Invitations were sent to FTOC members, with three of them attending. The workshop's duration was two days with the first day focusing on the pilot project itself and the second day presenting a broad technology discussion with presentations made by major national/international system houses and blowing agent manufacturers.

1. Introduction

Common technologies for replacing HCFC-141b in PU foams have been limited to water/isocyanate (sometimes combined with enhancements such as super-critical CO_2, formic acid, etc.), hydrocarbons and HFCs. Water has limitations in thermal insulation applications; HFCs usually have high GWP values and hydrocarbons are high in investment costs. There is therefore need to assess other potential alternatives and, therefore, to investigate emerging technologies on their technical merits, cost, availability, sustainability and environmental performance. Decision 55/43 of the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol ("MLF") reflects this by promoting pilot projects aimed at validating technologies in a developing country ("A5") context. The detailed objectives of such projects would be to:

- Develop, optimize and validate the use of alternative blowing agents or technologies in polyurethane foam applications meeting local and international safety standards;
- Demonstrate these technologies in a limited amount of downstream operations;
- Transfer the technologies to interested stakeholders, such as system houses and individual downstream users through workshops and investment projects.

UNDP has prepared six pilot projects which may cover substantially all current commercially available products that have potential or have been proven as blowing agent in foams but have not yet been assessed in an A5 context or that could be improved upon. These technologies are:

Substance	Sub-Sector	Country	Status	Justification
Supercritical CO_2	SPF	COL	Implementing *	Evaluation in thermal insulation applications
Hydrocarbons	RPF, ISF	EGY	Completing	Evaluation of cost saving options
Methyl Formate	RPF ISF FPF	BRA/MEX	Completing	Validation of a commercial available product
Methylal	RPF ISF FPF	BRA	Completed	Validation of a commercial available product
HFO-1234ze	XPS	TUR	Implementing	Validation of a commercial available product
CO_2/Methyl Formate co-blowing	XPS	CHI	Recently approved	Evaluation of performance for XPS Foam Boards and validating XPS extrusion equipment redesign

**Project approved as part of Japan Bilateral Cooperation. UNDP is implementing this project in behalf of Japan. There is also a World Bank Demonstration Project for sprayfoam in China with undefined technology choice*

There are other emerging HCFC replacements that are not yet commercially available. Most of these are based on unsaturated HFCs, also called hydrofluoroolefins or HFO's and mainly geared towards replacement of (saturated) HFCs in developed countries. They share low/no flammability, zero or insignificant ODP and insignificant GWPs as the following overview shows:

	HBA-2[1]	FEA-1100[2]	AFA-L1[3]
Chemical Formula	n/k	n/k	n/k
Molecular Weight	<134	161-165 (est.)	<134
Boiling point (^{0}C)	>15 <32	>33	>15 <30
Gas Conductivity (mWm^{0}K at 10 ^{0}C)	n/k	10.7	10
Flammable limits in Air (vol. %)	None	None	None
TLV or OEL (ppm; USA)	n/k	n/k	n/k
GWP (100 y)	<15	5	<15
ODP	0	0	0

[1] Honeywell [2] DuPont [3] Arkema

These chemicals may not be commercially available in the A5 markets within the next 2-3 years and that will be too late for application in projects for compliance with the HPMP Stage-I targets. From the mentioned pilot projects, the assessment of the use of methyl formate (MF) in non-continuous PU applications has been technically completed while the assessment of cost-effective HC technologies, the use of methylal and the use of HFO-1234ze are in the final stages with the experimental work done.

This particular pilot project—the use of methylal ("ML")—has been designed around Arinos Quimica Ltda ("Arinos")/Brazil, a large independent system house producing PU systems covering most PU applications, with input from Lambiotte & Cie/Belgium, a major supplier of methylal and a proponent for its use in PU foams as well as Dow-Brazil, which conducted most product testing. The application of methylal is shoesoles has been undertaken by Zadro, a system house in Mexico, specialized in this application.

To assure that methylal technology would be commercially available world-wide, UNDP has assessed its supply scenario as well as other potential barriers such as application patents.

Supply scenario – methylal is offered by manufacturers in Belgium, England, India, Korea and China. From these manufacturers, the only one that researched its use in PU foam applications and is actively marketing this is Lambiotte & Cie. These efforts have resulted in its use in around 20 European countries. In most cases its use is as a co-blowing agent in conjunction with other HCFC replacement such as hydrocarbons (HCs) and hydrofluorocarbons (HFCs). While this demonstration project undertaken in two large Latin American countries had been successful, the application of methylal technology should be carefully evaluated in the context of the local situation prevailing in each country.

Application patents – methylal has been patented for a multitude of narrowly defined PU applications, going back as far as 1995. None of these patents can claim effective and comprehensive intellectual rights on the use of methylal in PU foams and therefore the technology is considered free to use (source Lambiotte).

This assessment addresses in sequence

- Health, safety and environmental considerations,
- Processability, including stability, compatibility shipping and storage
- System composition information
- Overview of physical properties obtained from trials for different applications
- Indicative conversion costs
- Conclusions and recommendations

UNDP acknowledges with appreciation the cooperation extended by the project partners: Arinos, Lambiotte, Zadro and Dow do Brasil.

2. Design

PU foams are used in applications with different formulations. The original 18 applications as mentioned in the approved version of the project document have been narrowed down to 16 applications that use currently HCFC-141b. Under this project, these applications have been evaluated on the potential use of methylal as blowing agent with HCFC-141b as baseline technology to compare with. The different activities consisted of:

- Acquisition of the necessary testing/prototyping equipment;
- Optimization and validation of all 16 formulations on prototyping equipment;
- Development of safe practices meeting national and international standards for the transportation, storage and use of methylal in system houses and of methylal-containing systems at SMEs;
- Dissemination of the experience gained through a workshop.

Changing blowing agents, which are essential components in foam formulations, requires determination of baseline values for critical properties. Some are general in nature but others are specific as the following list shows:

Foam type	Application	Critical Properties	Relevant Tests
Integral Skin and Microcellular Foams	Flexible	Friability, surface	Visual (pinhole count) Abrasion, tear resistance
	Shoe soles		
	Structural (rigid)		
	Semi-flexible		
Rigid Foams	C/D refrigeration	Insulation, adhesion, dimensional stability, water permeability resistance	K-Value/peel strength (sometimes(heat loss, dimensional stability, closed cell content
	Water heaters		
	Trucks		
	Blocks/panels		
	Spray		
	Thermoware		
	PIR		
Semi-Rigid Foams	Packaging foam	Shock absorption	Drop test (hand)
Flexible Foams	Flexible molded	Appearance, touch	ILD/CLD (mostly by hand)
	Hyper-soft slabstock		
	Viscoelastic molded	Slow recovery	Recovery modulus (mostly by hand)
	Viscoelastic slabstock	Slow recovery	

Many companies and their suppliers do not conduct testing on properties of their foams on a regular base—or not at all--nor do they set standards. In such cases, rather than testing on meaningless properties, it has been deemed more important that the user expresses its agreement (in writing) with the quality and performance of the methylal-containing foam. These letters are compiled in **Attachment VIII**.

However, it is generally preferred to determine baseline data on critical properties against which the new foams can be objectively compared. It is emphasized that this assessment serves a very practical purpose which is to

Determine the extent to which methylal can be satisfactorily used in MLF-funded HCFC phase-out projects and, in this way, avoid unexpected setbacks in project implementations

This assessment does not include an exhaustive investigation into the way the technology works. It does, however, include back-to-back testing with the technology it replaces as well as review of existing data, specifically on health, safety and environment. The term *“**evaluation**”* **or** *“**assessment**”* therefore better describes the task at hand than the more formal/legal term *“**validation**”*.

Every application started with the development of laboratory formulations using methylal as auxiliary blowing agent (ABA). When these formulations were deemed acceptable, they were applied in machine trials. While initial trials were done as the system house, UNDP and Arinos decided that optimization together with customers would be more effective than prototyping at the system house only. Accordingly, formulations developed by Arinos and initially optimized at their facilities have been further optimized at customer level. The customers confirmed in writing if and when the formulation met their minimum requirements.

Arinos was not able to source an independent physical testing laboratory in Brazil. It found Dow Chemical do Brasil, which has in Brazil a new, fully equipped and ISO-9001 certified PU testing center, willing to perform the testing.

For more details, it is referred to the approved version of the project document (**Attachment I**).

3. Implementation

The project was approved at the 58th ExCom meeting in July 2009. Funding was received in October 2009 and the project started in earnest January 2010. The list of applications was first reviewed on work already completed (to save time, Arinos started immediately after project conception) and on the potential to combine applications based on same or very similar formulations.

Safety, health and environmental information on methylal are abundant. However, there are no industrial hygienic data that relates specifically to its use in PU foams. Therefore, emission monitoring data have been included in the assessment program. Based on methylal's relatively inert behavior it would not be likely that its use impacts structural foam properties. Critical issues to be addressed would therefore be

- Flammability,
- Workplace emissions and
- (Thermal) insulation value.

As the latter is not an issue with non-insulating foams, and these also use generally low levels of auxiliary blowing agents—decreasing the likelihood of adverse flammability and emission conditions—the applications template was functionally rearranged as follows:

Foam type	Application		Critical Properties	Developed/tested
Non Insulating Foams	Integral skin foams	Flexible	Friability, surface	√
		Shoe soles	Surface	√
		Structural (rigid)	Surface	√
		Semi-flexible	Surface	√
	Flexible foams	Flexible molded	Appearance, touch	√
		Hyper-soft block	Appearance, touch	√
		Viscoelastic molded	Slow mechanical recovery	√
		Viscoelastic block	Slow mechanical recovery	√
	Semi-rigid foams	Packaging foam	Shock absorption	√
Insulating foams	Rigid PU/PIR foams	Refrigeration	Insulation, adhesion, dimensional stability, water permeability	√
		Water heaters		
		Trucks		
		Blocks, Panels		
		Spray		
		Thermoware		
		PIR Blocks		

As soon as an application development was completed, samples were forwarded for physical testing. By early 2011, formulation development and optimization was completed and by August 2011 testing was finalized. However, due to relocation of Dow's laboratory, some samples were up to 10 months old when finally tested and retesting on fresh samples was required. This was completed mid-November. Arinos commissioned an industrial hygienic survey to assess methylal emission concentration during system blending. UNDP requested system processing to be included but this was not followed up on. The same data can also be used to assess the flammability of process emissions.

Methylal is also recommended in combinations with other blowing agents, such as HFC-365mfc and cyclopentane. This aspect has not been assessed in this project as its application concerns more developed countries than developing ones—the target of this assessment.

The pilot project for the evaluation/assessment of methylal as approved by the Executive Committee included a workshop to disseminate the results of the project. In conformity, a workshop was held in Sao Paulo, Brazil at the 6th and 7th of December 2011, with the participation of 108 attendants from 12 system houses from Brazil (being eight A5 owned: *Amino, Arinos, Ariston, M.Cassab, Polisystem, Polyurethane, Purcom and Utech*; and four non-A5: *Bayer, BASF, Dow and Huntsman*); from 13 foam manufacturing enterprises from Brazil and from Jamaica and Trinidad & Tobago; representatives from five Article 5 countries (*Colombia, Panamá, Paraguay, Peru and Jamaica*); representatives from UNDP, UNEP and GIZ ; three Brazilian industry associations (*Abripur, Abiquim and Abrava*), eight blowing agent manufacturers/distributors (*from Brazil, Belgium and United States*) and six foam dispenser manufacturers. Also, invitations were sent to FTOC members, with attendance of three of them. The workshop consisted of two days where the first day was focused in the pilot project itself, and its findings. The second day involved a broad technology discussion with presentations made by the major national and international system houses and blowing agent manufacturers.
*The Agenda and the presentation given in the workshop can be downloaded at:

http://www.protocolodemontreal.org.br/eficiente/sites/protocolodemontreal.org.br/pt-br/site.php?secao=eventos&pub=224

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[1] *The Agenda and the presentation given in the workshop can be downloaded at:
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4. Outcomes

Methylal, also called dimethoxymethane, belongs to the acetal family. It is a clear, colorless, flammable liquid with a relatively low boiling point and a sweet odor. Its primary use is as a solvent in the manufacture of perfumes, resins, adhesives, paint strippers and protective coatings. It is moderately soluble in water (33 % by weight) and miscible with most common organic solvents. A Material Safety Data Sheet (MSDS) prepared by Lambiotte & Cie and OSHA's Occupational Health Guideline for methylal are attached (**Attachment II**). There are many MSDS available from other suppliers, traders and independent institutions, which provide essentially the same information but Lambiotte follows the Global Harmonization System (GHS)—which will be the future standard for OSHA as well. Following data on physical properties are compared with HCFC-141b, which it seeks to replace:

Property	Methylal	HCFC-141b
Appearance	Clear liquid	Clear liquid
Boiling point	42 °C	32 °C
LFL/UFL	2.2-19.9 %	7.6-17.7
Vapor pressure	400 mm Hg @ 20 °C	593 mm Hg @ 25 °C
Lambda, gas	14.5 mW/m.k@ 42 °C*	10.0 mW/m.k @ 25 °C
Auto ignition	235 °C	>200 °C
Specific gravity	0.821 @ 20 °C	1.24
Molecular weight	76.09	117
ODP	0	0.11
GWP	Negligible	630

*Extrapolation at 25 °C would be ~ 11

Below is a comparison with other, common, foam blowing agents on the most relevant properties:

Property	HCFC-141b	Methylal	Cyclo Pentane	HFC-245fa	Methyl Formate
LFL/UFL (%)	7.3-16.0	1.6/17.6	1.4-8.0	None	5.0-23.0
Molecular Weight	117	76	70	134	60
Gas Conductivity (mW/m°K)	10 (25°C)	14.5 (42°C)*	11 (10°C)**	12.5 (24°C)	10.7 (25°C)
TLV/OEL (ppm)	500 (TLV)	1,000 (TLV)	600 (TLV)	300 (WHEEL)	100 (TLV)
Global warming potential (100 y; IPCC-1996)	630	Negligible	11	820	Negligible
ODP	0.11	0	0	0	0
Photochemical Ozone Creation Potential (MIR)	<0.01	0.89	2.39	0.00	0.06

*Extrapolation at 25 °C would be ~ 11; **extrapolation at 25 °C would be ~13.9

Methylal is offered in different purities. It is recommended (Lambiotte) that the pure grade suits its use as blowing agent best:

Compound	Cosmetic Grade	Anhydrous Grade	Pure Grade	Technical Grade
Methylal	**99.5 % min.**	**99.9 % min.**	**99.5 % min.**	**93 % min.**
Methanol	< 1 ppm	< 0.05 %	< 0.05 %	6.5 % max
Formaldehyde	< 1 ppm	< 0.005 %	< 0.0005 %	< 0.02 %
Water	< 0.5 %	< 0.03 %	< 0.5 %	< 0.25 %

4.1 Health, Safety and Environment (HSE)

4.1.1 Health

Methylal's toxicity profile compares as follows with HCFC-141b:

	Methylal	**HCFC-141b**
TLV (TWA)	1000 ppm	500 ppm
TLV (STEL)	1250 ppm	500 ppm
Acute toxicity (oral)	LD50 5.6 g/kg (rat)	LD50 5 g/kg (rat)
Sub-acute inhalation	NOEL = 4,000 ppm (8 x 6 h)	20,000 ppm
Sub-chronic inhalation:	NOEL = 2,000 ppm	20,000 ppm
Eye irritation:	minor to moderate	minor to moderate
Skin irritation:	none to slight	none to slight
Dermal sensitization:	not allergenic	non allergenic
Ames test:	no mutagenic activity	no mutagenic activity

To assess actual emissions compared to the applicable TWA and STEL, a workers exposure evaluation has been commissioned. This evaluation was conducted by Environ/San Bernardo-SP at the Arinos facility, following the Brazilian legal standard as published in Directive 3214/78 of the Ministry of Labor in its NR-9. The values measured show the following range:

Personal Sampling (production area operators)	3.4 – 17.3 ppm
Area Sampling (blending and weighing area)	2.6 – 6.5 ppm

This is between 0.3 - 1.7 % of the TLV (TWA) and between 0.2 – 1.4 % of the TLV (STEL). The evaluation, which in its full text is attached (**Attachment-III**) concludes that:

The Occupational Quantitative Assessment of Methylal in the atmospheric air at Arinos showed that all samples are lower than the action level from TLV-TWA (ACGIH)

Although the evaluation indicates that no IH or flammability issues are to be expected when preparing ML-based systems—the only operation that processes pure ML—an application specific audit for downstream users needs to confirm this. Methylal users can for relatively moderate costs (around US$ 2,500/unit) conduct their own compliance testing with an electronic monitor made by new Cosmos/Japan:

METHYYLAL EMISSONS DETECTOR 0-2,000 ppm

An extensive toxicological profile is attached (**Attachment-IV**).

4.1.2 Safety

Methylal is classified as highly flammable (R11) and an eye irritant (R19). Some MSDS mention also R36 (might form explosive peroxides). However, Lambiotte reports from its tests that methylal does **not** form any peroxides (*0 ppm of peroxides after 1143 days under air or under nitrogen*) so that this statement, while tentative, appears incorrect. Following flammability related data are available:

flash point (open cup):	-18°C (-0.4°F)
auto-ignition temperature:	237°C (458.6°F)
lower/upper flammability limits:	1.6 % vol (LFL)/17.6 % vol (UFL)

Methylal used as proposed will reduce the related risk at downstream users by preblending at supplier level (system houses). Meeting applicable industrial hygienic thresholds will keep emissions well under the LFL (STEL = 1250 ppm = 22 % of LFL). Moreover, in view of the outcome of the Environ industrial hygiene evaluation, it is not expected that at any time a methylal concentration of 17.3 ppm would be exceeded. This translates into expected airborne methylal concentrations to be less than 0.03% of the LFL.

As mentioned, there are no data on explosion risks. Essential elements required to trigger an explosion are fuel, air, an ignition source and containment. Fuel could be pure methylal or a methylal-based fully formulated system. To bring the latter to explosion at downstream user level is not possible as long as, as mentioned before, industrial hygienic thresholds are respected—but the margin at TLV level—while unlikely to be reached—Is not a very comfortable one as it is common standard to set LFL alarm levels on 20-35%. Aside from the challenge to ignite the polyol mixture, the heat of combustion is very low so that the necessary pressure built-up in containment will not easily be achieved. **Attachment V** addresses flammability issues more in detail.

Notwithstanding the very remote likelihood of a sustainable flammable situation—much less even an explosion risk—it is advised to follow recommendations for the handling of flammable liquids as, regardless of the likelihood of explosion risk, fully blended methylal-based systems exceeding 2-7.5 php in polyol and/or isocyanate are flammable and might require compliance with applicable local regulations.

4.1.3 Environment

Methylal has a relatively good eco-toxicological profile:

	Methylal	**HCFC-141b**
Daphnids, fish (Brachydanio Rerio)	no effect	31.2 – 126 mg/L
Biodegradability (ISO/DIS 8192)	biodegradable	not biodegradable

Its atmospheric chemistry is also favorable, with a relatively low photochemical ozone creation potential (POCP), a short atmospheric residence period of 2-5 days, a negligible global warming potential (GWP) and—because there are no halogens incorporated in the molecule—zero stratospheric ozone depletion potential (ODP).

Lambiotte commissioned an eco-toxicological profile, which is attached (**Attachment VI**).

4.2 System Processability

4.2.1 Shipping, Handling and Storage

The proper shipping name for methylal is UN1234 METHYLAL, 3, II. It is highly flammable and needs to be labeled accordingly:

Signal Word: **Danger**
Hazard Statement: **Highly flammable liquid and vapor**

The label as shown belongs to the labeling elements of the “Global Harmonization System (GHS) for Flammable and Combustible Liquids”, an international hazard classification system proposed under the guidance of the United Nations Subcommittee for GHS, and adopted—or in the process of adoption—by an ever-growing group of countries, including Brazil, the EU and the USA. Methylal users should, however, also check—and comply with—local regulations as they may have different requirements and the most stringent should be applied.

Shipment and storage of methylal can be carried out in carbon steel vessels or containers. No special material is required. Carbon steel is also acceptable for storage and piping. Methylal has a very low viscosity which causes the need to recalibrate viscosity sensitive metering equipment (such as low-pressure pumps) but also allows for gravity or low pressure transfer (around 0.7 bar). Pump transfer is, however, considered more suitable.

4.2.2 Stability

Following stability data have been provided by Arinos and Lambiotte:

• Thermal stability	- Stable for 7 days at 200 ^{0}C
• Peroxide building	- No formation of peroxides has been detected
• Hydrolysis	- Stable under neutral/alkaline conditions (polyols are slightly alkaline) - The pH of ML systems matches approximately those of HCFC-141b - Very slow (>1 year) hydrolysis under acid condition
• Corrosion	- No corrosivity determined

Manufacturers typically offer shelf lives of 6 months after date of manufacturing for their systems, if stored in original, unopened containers at temperatures typically between 10°C and 30°C. Methylal-based systems as offered by Arinos are meeting this shelf life standard.

Moreover, internal tests at Arinos show no change in activity of retained formulation samples stored for at least twelve months under standard conditions.

4.2.3 Compatibility

Methylal is miscible with all types of polyols commonly used in PU foam applications. This is an advantage compared to hydrocarbons which require sometimes significant polyol adjustments to overcome solubility issues and mix rather as dispersions than being truly dissolved. HCFC-141b-based systems are completely miscible but show some instability when blended in large concentrations. It took the industry time to conclude that the potent solvent character of this substance limits its use in a system. Liquid HFCs show limited miscibility in some polyols.

All application trials at Arinos have been conducted using the same chemicals as with HCFC-141b. From this, it can be concluded that the replacement of HCFC-141b with methylal does not require qualitative changes in chemicals. However, different polyols and/or additives could impact the flammability of the systems. This is not entirely negative as it also creates an option for optimization. Preliminary studies show that polyols of higher viscosity give systems with higher flashpoints. Also, because methylal is miscible in polyols as well as isocyanates, the option exists to reduce flammability by blending in both system components. These potential options for optimization in fire behavior, while highly recommended, need to be conducted by individual system houses and are beyond the scope of this assessment.

Methylal also acts as a potent viscosity reducer, typically cutting polyol viscosities in half or even less. This accommodates processing of higher viscosity blends such as in shoesoles.

4.3 System Composition

Following general rules apply when changing from HCFC-141b to methylal as auxiliary blowing agent (ABA):

- Equimolar replacement would require 1 kg methylal to replace 1.54 kg HCFC-141b;
- Because of the strong solvent effect of HCFC-141b this ratio can, however, change for high-ABA formulations to 1:1.7 or even 1:1.9. In other words, ML is more effective in high ABA formulations;
- If the objective would be to keep the methylal system non flammable, the maximum amount of methylal would be between 2 and 5 php—depending on the choice of polyol—which is equivalent to 3.5—8.5 php HCFC-141b. Increased water levels or blending of ML in isocyanate could provide additional blowing;
- If flammability is accepted—and accounted for in safety measures—any amount of HCFC-141b in a commercial formulation can be replaced by the equivalent amount of ML without significant other formulation changes;
- Blends of polyols with a high amount of methylal still may be exempt from flammability labelling because they show low combustion tendencies. In the EU, as well in countries with similar applicable regulations, no flammable labelling is needed if the flash point of a blend is between 21°C and 55°C but the blend doesn't contribute to the combustion.

Attachment VII contains sample formulations for different applications. These formulations should be considered guidelines as each commercial application needs its own optimization.

4.4 Foam Properties

Determining the acceptability of an HCFC-141b replacement technology includes measuring of relevant physical properties before and after replacing HCFC-141b. A technology is deemed acceptable for a particular application if the physical properties are within a predetermined range (generally 10%, but the downstream user has the last word) from the original properties using HCFC-141b. For subjective issues such as appearance and for applications not requiring testing, the downstream user's determination of the quality is the ultimate criterion of acceptability.

As final trials have been conducted at customer level, these customers have been requested—and complied with—providing a declaration stating agreement with the methylal-base foams in their particular application. For all applications, such declarations have been received and are on file.

All development and initial optimization trials have been conducted at Arinos' Development Center. Final optimization and validation took place at selected downstream users. Physical testing has been conducted at the Arinos and Dow Brazil facilities. The development and testing of PU shoesoles has been performed through Zadro/Mexico. Individual test protocols are on file.

Test results/discussions have been categorized as follows:

- Non Insulation Foams 1 Hypersoft Foams (blocks)
  2. Viscoelastic Foams (molded)
  3. Viscoelastic Foams (blocks)
  4. Flexible Foams (molded)
  5. Integral Skin Foams (flexible)
  6. Integral skin Foams (semi-rigid)
  7. Integral Skin Foams (rigid/structural)
  8. Microcellular foams (shoesoles)
  9. Packaging foams (semi-rigid)

- Insulation Foams 1. Appliance Foams (rigid injection)
  2. Water Heaters
  3. Panels, Blocks
  4. Transportation
  5. Thermoware
  6 Polyisocyanurate Foams (PIR)
  7. Spray foams

In many cases the ML densities did not quite match the ones for HCFC-141b. The delay in testing, based on Dow's laboratory relocation caused a time crunch that did not allow further optimization. However, this is not an issue inherent to the use of ML but just misjudging of the impact of converting from laboratory (hand-mixed) foams to machine trials.

4.4.1 Non Insulating Foams

4.4.1.1 Hypersoft Foams (blocks)

- Assessment Letter: Techfoam
- Machine: Boxfoam
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m3	25,3	25,7
Resilience	%	38	37
Tensile Strength at break	kPa	127,6	139,5
Tear Propagation	N/mm	526,3	530,6
Elongation at break	%	504,3	483,4
Compression set 50%	%	5,4	5,6

ILD 25%	N	9,7	8,3
ILD 40%	N	13,7	10,9
ILD 65%	N	22,4	19,6

4.4.1.2 Viscoelastic Foams (molded)

- Assessment letter: Vittaflex
- Machine Low Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m^3	48,6	46,7
Resilience	%	12	10
Tensile Strength at break	kPa	101,4	109,2
Tear Propagation	N/mm	518,2	545,3
Elongation at break	%	494,8	461
Compression set 50%	%	3.7	3.6
ILD 25%	N	36	31
ILD 40%	N	46	43
ILD 65%	N	73	72

4.4.1.3 Viscoelastic Foams (block)

- Assessment letter: Techfoam
- Machine: Boxfoam
- Test results:

Medium Density

1) Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m^3	36	42,5
Resilience	%	6	6
Tensile Strength at break	kPa	77,7	63,6
Tear Propagation	N/mm	378	267,9
Elongation at break	%	234,3	284,3
Compression set 50%	%	0,94	0,61
ILD 25%	N	41	35
ILD 40%	N	58	49
ILD 65%	N	105	92

Low Density

2) Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m^3	27,7	26
Resilience	%	4	4
Tensile Strength at break	kPa	55,3	58,1
Tear Propagation	N/mm	296,4	260,5
Elongation at break	%	278,1	314

Compression set 50%	%	1,6	2,1
ILD 25%	N	6	6
ILD 40%	N	14	13
ILD 65%	N	36	31

4.4.1.4 Flexible Foams (molded)

- Assessment letter: Brastec Florense
- Dispenser: Low Pressure
- Test results:

Properties	**Unit**	**HCFC 141b**	**Methylal**
Density (foam)	Kg/m^3	38,3	40,1
Resilience	%	46	46
Tensile Strength at break	kPa	130,9	126,8
Tear Propagation	N/mm	614,5	575,5
Elongation at break	%	123,8	128,6
Compression set 50%	%	11	9,83
ILD 25%	N	150	151
ILD 40%	N	236	233
ILD 65%	N	536	527

4.4.1.5 Integral Skin Foams (flexible)

- Assessment Letter: Blitz
- Machine: High Pressure
- Test results:

Properties	**Unit**	**HCFC 141b**	**Methylal**
Entire Sample			
Molded Density	Kg/m3	348,6	356,7
Hardness	Shore A	52	50
Resilience	%	34	35
Foam Core			
Internal Density	Kg/m^3	244,2	265,3
Tensile Strength	kPa	238	241
Elongation	%	66	63
Tear Strength	N/mm	1,150	1,090
Compression Set (50%)	%	19	21
Skin Only			
Tensile Strength	kPa	975	980
Elongation	%	77	78
Tear Strength	N/mm	3780	3810

4.4.1.6 Integral Skin Foams (semi-rigid)

- Assessment Letter: Blitz
- Machine: High Pressure
- Test results: No tests are required in Brazil

4.4.1.7 Integral Skin Foams (rigid/structural)

- Assessment Letter: Blitz
- Machine: High Pressure
- Test results: No tests are required in Brazil.

4.4.1.8 Microcellular Foams (shoesoles)

- Assessment Letter: Test report Zadro/Ciatec (accredited test center)
- Machine: Low-pressure
- Test results:

Property	**All**	**R-095**	**R-096**	**R-099**	**QZCT15**	**Test Method**
Type	**types**	**SPORT**	**TRAVEL**	**RIGID**	**SEMI-RIGID**	
Blowing Agent	**141b**	**ML**	**ML**	**ML**	**ML**	
Density (kg/m^3)	<450	450	450	400	400	DIN 53420 ASTM D-792
Tear resistance (kgf/cm)	>6*	25.4	41.6	n/a	n/a	DIN 53507 ASTM D-624
Abrasion Resistance (mg, maximum)	<350	161.3	242.3	96.5	232.8	DIN 42516 ASTM D-1044
Flex Resistance (%, 30,000 cycles)	<200*	0	0	n/a	n/a	DIN 53543 ASTM D-1052

* only applicable for flexible shoesoles

4.4.1.9 Packaging Foams (semi-rigid)

- Assessment Letter: Poliuretanos do Brasil
- Machine: Low Pressure
- Test results: No tests are required in Brazil.

4.4.2 Insulation Foams

4.4.2.1 Appliance Foams (rigid injection)

- Assessment Letter: MF Cozinhas
- Machine: High Pressure
- Test results:

Properties	**Unit**	**HCFC 141b**	**Methylal**
Density	Kg/m^3	38,2	40,6
K factor	mW/mK	22,7	23.7

Compression set 10%	kPa	197,7	183,5
Compression set 10%	kPa	195,3	182,6
Dim. Stability (+70 C)			
side 1 max	%	6,97	1,67
side 1 min	%	-0,24	-0,81
side 2 max	%	-0,81	-0,90
side 2 min	%	-0,31	0,05
thickness max	%	0,73	4,78
thickness min	%	-0,25	0,13
Dim. Stability (-20 C)			
side 1 max	%	-0,16	0,41
side 1 min	%	-0,01	-0,01
side 2 max	%	-0,59	0,28
side 2 min	%	-0,14	-0,03
thickness max	%	-5,87	-0,92
thickness min	%	-0,52	-0,28

4.4.2.2 Water Heaters

- Assessment Letter: Heliotek
- Machine: High Pressure
- Test results:

Properties	**Unit**	**HCFC 141b**	**Methylal**
Density	Kg/m^3	36.9	39.4
K factor	mW/mK	22,6	24.5
Compression set 10% (Pa)	kPa	249,9	236,8
Compression set 10% (Pe)	kPa	217,7	-
Dim. Stability (+70 C)			
side 1 max	%	0,85	-0,31
side 1 min	%	-0,11	-0,29
side 2 max	%	-0,35	-0,41
side 2 min	%	0,03	-0,28
thickness max	%	-4,53	-0,57
thickness min	%	-0,18	-0,55
Dim. Stability (-20 C)			
side 1 max	%	0,25	-0,10
side 1 min	%	0,06	-0,06
side 2 max	%	0,10	-0,07
side 2 min	%	0,03	-0,04
thickness max	%	0,21	-0,27
thickness min	%	0,04	-0,23

4.4.2.3 Panels, Blocks

- Assessment Letter: Politech
- Machine: Boxfoam
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m^3	43,7	43,0
K factor	mW/mK	22,2	25.1
Compression set 10% (Pa)	kPa	243,1	211,8
Compression set 10% (Pe)	kPa	276,5	262,9
Dim. Stability (+70 C)			
side 1 max	%	-1,19	-0,9
side 1 min	%	-0,09	-0,04
side 2 max	%	-0,44	-1,11
side 2 min	%	-0,01	-0,52
thickness max	%	-6,31	-2,85
thickness min	%	-0,91	1,18
Dim. Stability (-20 C)			
side 1 max	%	0,53	-0,08
side 1 min	%	-0,11	-0,02
side 2 max	%	-0,32	-0,32
side 2 min	%	0,05	-0,06
thickness max	%	6,21	-6,26
thickness min	%	0,05	-0,12

4.4.2.4 Transportation

- Assessment Letter: Furgões Roma
- Machine: High Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m^3	39,8	41.3
K factor	mW/mK	22,5	24.6
Compression set 10% (Pa)	kPa	174,4	172.1
Compression set 10% (Pe)	kPa	213,2	210.3
Dim. Stability (+70 C)			
side 1 max	%	-0,58	-0.64
side 1 min	%	-0,16	-0.18
side 2 max	%	-0,56	-0.67
side 2 min	%	-0,19	-0.22
thickness max	%	-4,11	-2.24
thickness min	%	2,32	1.82

Dim. Stability (-20 C)			
side 1 max	*%*	0,03	0.04
side 1 min	*%*	-0,01	-0.02
side 2 max	*%*	0,03	0.04
side 2 min	*%*	0,01	-.03
thickness max	*%*	0,09	0.12
thickness min	*%*	0,01	0.04

4.4.2.5 Thermoware

- Assessment letter: Soprano
- Machine: High Pressure
- Foam Tests:

Properties	**Unit**	**HCFC 141b**	**Methylal**
Density	Kg/m^3	36,9	39,4
K factor	mW/mK	22,8	24,2
Compression set 10% (Pa)	kPa	203,6	184,3
Compression set 10% (Pe)	kPa	189	158,9
Dim. Stability (+70 C)			
side 1 max	*%*	0,43	1,08
side 1 min	*%*	0,09	0,01
side 2 max	*%*	0,70	1,94
side 2 min	*%*	-0,02	0,06
thickness max	*%*	-1,25	-2,35
thickness min	*%*	-0,70	-0,63
Dim. Stability (-20 C)			
side 1 max	*%*	0,20	-0,15
side 1 min	*%*	0,02	-0,02
side 2 max	*%*	0,16	0,13
side 2 min	*%*	-0,02	-0,02
thickness max	*%*	-6,88	-1,33
thickness min	*%*	0,41	-0,07

4.4.2.6 Polyisocyanurate Foams (Blocks)

- Assessment Letter: Politech
- Machine: Boxfoam
- Test results:

Properties	**Unit**	**HCFC 141b**	**Methylal**
Density	Kg/m^3	41,5	42,5
K factor	mW/mK	25,1	27.2
Compression set 10% (Pa)	kPa	312,8	169,8

Compression set 10%	kPa	321,1	148,4
Dim. Stability (+70 C)			
side 1 max	%	-0,89	0,43
side 1 min	%	-0,08	0,02
side 2 max	%	-1,47	1,65
side 2 min	%	-0,84	0,36
thickness max	%	-3,00	-3,55
thickness min	%	-0,59	0,25
Dim. Stability (-20 C)			
side 1 max	%	-0,05	0,15
side 1 min	%	0,03	-0,01
side 2 max	%	0,04	0,10
side 2 min	%	0,02	0,02
thickness max	%	-0,38	7,39
thickness min	%	-0,13	0,01

4.4.2.7 Spray Foams

- Assessment Letter: Isar
- Machine: High Pressure
- Test results:

Properties	**Unit**	**HCFC 141b**	**Methylal**
Density	Kg/m3	28,6	31,5
K factor	mW/mK	21,03	23,15
Compression set 10% (Pa)	kPa	198,6	194,3
Compression set 10% (Pe)	kPa	183,5	181,9
Dim. Stability (+70 C)			
side 1 max	%	-0,56	-0,62
side 1 min	%	-0,15	-0,17
side 2 max	%	-0,54	-0,65
side 2 min	%	-0,18	-0,21
thickness max	%	-3,98	-2,17
thickness min	%	2,25	1,76
Dim. Stability (-20 C)			
side 1 max	%	0,04	0,05
side 1 min	%	-0,01	-0,03
side 2 max	%	0,04	0,05
side 2 min	%	0,01	0,04
thickness max	%	0,12	0,16
thickness min	%	0,01	0,05

Note: because of shortness in time, this application, a minor application in Brazil, was not completely optimized.

5. Conversion Costs

Following are tentative cost templates to calculate incremental cost of conversion from HCFC-141b to methylal-based foams. It should be pointed out that equipment and chemical cost can differ significantly from country to country, from time to time, and are also subject to economy of scale considerations.

5.1 Incremental Capital Costs

ENTITY	ACTION	CALCULATION	Comment
System House	Explosion proofing of blending tanks	AA x 30,000	As for methyl formate
System House	Nitrogen dispenser	BB x 8,000	
System house	ML vapor monitors	2 x 2,500	To monitor IH compliance
System House	Spray/PIP safety package	CC x 7,500	Exhaust, grounding
System House	LPD/HPD safety package	DD x 15,000	Exhaust, grounding
System House	Pycnometer (closed cell tester)	10,000	As FSPOP project template
System House	Portable K-factor tester	10,000	
System House	Refractometer (test chemical purity)	10,000	
System House	Small rent-out dispenser	EE x 25,000	
System House	Project Management	FF clients @ 1,000	
System House	Monitoring & technology transfer	30,000	
System House	Contingencies	10% of capital costs	
Customers	ML vapor monitor	FF x 2,500	To monitor IH compliance*
Customers	Spray/PIP safety packages	GG x 7,500	Exhaust, grounding
Customers	LPD/HPD safety package	HH x 15,000	Exhaust, grounding
Customers	New Dispensers	II x 35,000	Include safety packages
Customers	Trials, testing, training,	KK machines @ 3,000	As in approved projects
Customers	Contingencies	10% of capital costs	

* This monitor could be deleted in case the supplier or a certified third party conducts an industrial hygiene survey that proves the TLV under production conditions to be less than 20% of the TLV. The cost of such a survey, however, might exceed to cost of a monitor

5.2 Incremental Operating Costs

Following is an example of an incremental cost template for IOCs. Prices are for illustration only. Three system experts were asked to convert a given HCFC-based formulation to MF. The results are quite similar. The last formulation leaves the chemical ratio the same, which is required for sprayfoams.

CHEMICAL	PRICE (US$/kg)	BASELINE		Expert A		Expert B		Expert C		Cost Base	
		%	Cost	%	Cost	%	Cost	%	Cost	%	Cost
Polyol	3.20	38	1.22	40	1.28	40	1.28	42	1.34	42	1.34
Isocyanate	3,00	50	1.50	52	1.56	54	1.62	50	1.50	50	1.50
HCFC-141b	2.40	12	0.29	--	--	--	--	--	--	--	--
Methylal	4.00	--	--	8	0.32	6	0.24	8	0.32	8	0.32
Cost			3.01		3.16		3.14		3.16		3.16
Difference			**Base**		**0.15**		**0.15**		**0.15**		**0.15**

6. Conclusions

Based on the information presented in this report and its attachments it is concluded that:

6.1 Health, Safety, Environment

- The use of methylal does not create incremental health concerns;
- Flammability is an inherent safety risk and, although on downstream user level drastically mitigated through the use of preblended systems, requires safety measures as outlined in **Attachment V**;
- Methylal-based systems do not pose an environmental hazard based on current knowledge.

6.2 System Processability

- Shipment and storage of pure methylal must comply with its flammability status (GHS Category 2—highly flammable liquid and vapor);
- No special considerations are required for fully formulated systems with less than 2% methylal (polyols) or less than 2% methylal (isocyanates). Systems containing 2-5 php methylal need individual consideration and above that level, compliance with GHS category 2 or 3 is required. Local regulations have to be consulted in addition;
- Methylal-based systems for all applications are stable;
- Methylal and methylal blends are not corrosive;
- There are no compatibility issues of methylal with polyols and/or additives. However, it is recommended that when designing conversion projects, the compatibility of baseline polyols will be carefully checked and the impact on flammability characteristics determined;
- The shelf life for methylal meets the commercial requirement of at least 6 months under standardized conditions

6.3 Foam Properties

- Methylal-based non-insulation foams, regardless of application, match HCFC-141b foams;
- Methylal-based thermal insulation foams match HCFC-141b foams within a determined variation range in stability and density but carry a penalty in insulation value of up to 10 %. This is comparable with methyl formate while better than HCs and water-based systems;
- No data on long-term performance are as of yet available;
- Customers selected for performance trials—one per application—all expressed agreement with the performance of methylal-based PU systems.

6.4 Conversion Costs

Indicative conversion cost estimates by UNDP show modest capital and operating costs increases compared to other conversions from HCFC-141b.

It should be pointed-out, however, that capital and operating (chemical) costs can differ significantly from country to country and that these are also subject to economy of scale operations and location of the supplier

7. Overall Assessment

Following is a consolidated overview of the findings of this report:

Foam Type	Application	HSE	Assessment			
			Processing	Flamma/ bility	Physical Properties	Results
Non insulation foams	Flexible	+	+	+	+	+
	Shoe soles	+	+	+	+	+
	Structural (rigid)	+	+	+	+	+
	Semi-flexible	+	+	+	+	+
	Flexible molded	+	+	+	+	+
	Hyper-soft block	+	+	+	+	+
	Viscoelastic molded	+	+	+	+	+
	Viscoelastic block	+	+	+	+	+
	Packaging foam	+	+	+	+	+
Insulation Foams	Refrigeration	+	+	+/-	+/-	+/-
	Water heaters	+	+	+/-	+/-	+/-
	Trucks	+	+	+/-	+/-	+/-
	Blocks, Panels	+	+	+/-	+/-	+/-
	Spray	+	+	+/-	+/-	+/-
	Thermoware	+	+	+/-	+/-	+/-
	PIR	+	+	+/-	+/-	+/-

HSE + Good (Compliance with international standards)
Processing + Good (agreement as per customer who carried out the qualifying trials);
Flammability + Non flammable (Cleveland closed cup test; as per formulations in Annex VII)
+/- May be flammable (Cleveland closed cup test)
Phys. Properties + Good (agreement as per customer who carried out the qualifying trials based on +/- 5% range of results)
+/- Fair (acceptance is subject to company´s willingness to adopt a somewhat less favorable insulation value).
Source: Lambiotte / Arinos

Note on flammability tests – the tests typically used to determine flammability (open and closed cup tests0 are typically designed for transportation purposes and do not reflect very well danger in the workplace. For that reason, the EU has for processing purposes different tests, emphasizing the sustainability of a fire from emissions. ML-based systems with less that 8 php ML do pass such tests.

Based on this assessment, the results indicate that ML-based systems are an excellent HCFC-141b substitute for non-insulation PU foams.

They are less suited for the replacement of HCFC-141b in (thermal) insulation PU foams as they carry a penalty in insulation value of up to 10 %. Further optimization may reduce this—but unlikely will eliminate this penalty entirely.

Safe use of methylal as an alternative blowing agent to replace HCFC-141b in PU foam applications in MLF projects would have to be subject to the following conditions:

- Projects should preferably be implemented through local system houses to minimize safety risks at downstream users ;
- Project designers should ensure that:
  - Chemical compatibility is verified,

- Implications related to the flammable character of the substance are addressed as recommended in **Attachment V**:

SYSTEM HOUSES

- Proper personal protective equipment
- Closed blending containers, with a dry nitrogen blanket
- Explosion proof equipment (pump, agitator, light, heating/cooling)
- Electrically grounded equipment and drums (grounding clip)
- A methylal vapor sensor with alarm function set on 20% (= ~TLV)
- Adequate ventilation
- Meter Methylal under the level of the liquid to which it is being added
- Adherence to MSDS, OSHA and local guidelines

DOWNSTREAM USERS

- Proper personal protective equipment
- Electrically grounded equipment and drums (grounding clip)
- A methylal vapor sensor with alarm function set on 20% LFL (= ~TLV) LFL OR an industrial hygiene survey by supplier/certified third party
- Adequate ventilation
- Adherence to MSDS and local guidelines

ATTACHMENT I:
PROJECT DOCUMENT (APPROVED VERSION)

COUNTRY:	**Brazil**	**IMPLEMENTING AGENCY:**	**UNDP**

PROJECT TITLE:	**Pilot project to Validate Methylal as Blowing Agent in the Manufacture of Polyurethane Foams (Phase-I)**
PROJECT IN CURRENT BUSINESS PLAN:	**Based on ExCom Decision 55/43(e i-iii)**
SECTOR:	**Foams**
ODS USE IN SECTOR	
Baseline:	**N/A**
BASELINE ODS USE:	**N/A**
PROJECT IMPACT (ODP targeted):	**N/A**
PROJECT DURATION:	**9 months (Phase-I only)**
PROJECT COSTS:	**US$ 464,200 (Phase-I only)**
LOCAL OWNERSHIP:	**100 %**
EXPORT COMPONENT:	**0 %**
REQUESTED MLF GRANT:	**US$ 464,200**
IMPLEMENTING AGENCY SUPPORT COST:	**US$ 34,815 (7.5 %)**
TOTAL COST OF PROJECT TO MLF:	**US$ 499,015**
COST-EFFECTIVENESS:	**N/A**
PROJECT MONITORING MILESTONES:	**Included**
NATIONAL COORDINATING AGENCY:	**Ministry of Environment - MMA/PROZON**

Project Summary

Brazil became a Party to the Vienna Convention and Montreal Protocol on 19 March, 1990. Brazil also ratified the London, Copenhagen, Montreal and Beijing Amendments. The country is fully committed to the phaseout of HCFCs and willing to take the lead in assessing new HCFC phaseout technologies, particularly in the foam sector. It has a vibrant local PU system house system that caters to SMEs while all international PU chemical manufacturers are represented which concentrate on the larger users

The objective of this project is to develop, optimize, validate and disseminate the use of methylal in PU foam applications. Validating now can save a multiple of the validation costs in subsequent projects.

The project is divided in two distinct phases:

Phase-I:	development, optimization, validation and technology dissemination
Phase-II:	implementation in 15 downstream enterprises covering all relevant applications

At this stage funding only for Phase-I is requested. The costs Phase-II are included as a preliminary indicative estimate. The Phase-II costs will be updated after completion of Phase-I and submitted for approval in 2009. It is the intent that the UNEP Foams Technical Options Committee will be involved in the validation.

IMPACT OF PROJECT ON COUNTRY'S MONTREAL PROTOCOL OBLIGATIONS

This project is a pilot project aimed to validate a new HCFC phase-out technology and will contribute indirectly to the fulfillment of Brazil's Montreal Protocol obligations. If successfully validated, the technology will contribute to availability of cost-effective options that are urgently needed to implement HCFC phase-out, particularly at SMEs.

Prepared by: Rappa, Inc. **Date: May 2009**

PROJECT OF THE GOVERNMENT OF BRAZIL
PILOT PROJECT TO VALIDATE METHYLAL AS BLOWING AGENT IN THE MANUFACTURE OF POLYURETHANE FOAM (PHASE-I)

1. PROJECT BACKGOUND

This project has been prepared as response to the Executive Committee Decision 55/43 and it is part of a limited group of pilot validation projects being implemented by UNDP with the objective to develop, optimize and validate chemical systems for use with non-HCFC blowing agents. At its 56th meeting, November 2008, the Executive Committee approved the first two pilot projects (one in Brazil) that will address the validation of one of these technologies (methyl formate) in all relevant PU applications. The present project aims to undertake a similar process in Brazil with another technology (methylal). The other technologies that make part of this limited group of pilot validation initiatives are listed in Table 1 below and will be tested in other countries.

2. PROJECT OBJECTIVES

The objectives of this project are to:

1. Develop, optimize and validate the use of methylal as auxiliary blowing agent in polyurethane foam applications meeting local and international safety standards;
2. Demonstrate the technology in a limited amount of downstream operations;
3. Transfer the technology to interested stake holders, such as system houses and individual HCFC users, anywhere in the world.

3. INTRODUCTION

Current validated technologies for replacing HCFC-141b in foams are restricted to water/isocyanate, hydrocarbons and HFCs. With water non-performing in thermal insulation applications, HFCs being high in global warming potential and hydrocarbons high in investment costs, it is important to validate other options. ExCom Decision 55/43 reflects this by promoting pilot projects aimed to validate technologies. UNDP has followed recent developments in this industry very closely. Its evaluation also covered potential improvements on validated technologies that raise environmental concerns or are high in cost. Based on its findings it has prepared a total of five (5) pilot projects which may cover all commercially available products that have potential as blowing agent in foams but have not yet been validated in an A5 context. These technologies are:

SUBSTANCE	STATUS	COMMENTS
Hydrocarbons	To be submitted to the 58th ExCom	Evaluation of cost saving options
Methyl formate	Approved at the 56th ExCom	Technical validation of a commercial available product
Methylal	To be submitted to 58th ExCom	Technical validation of a commercial available product
Supercritical CO_2	Under development	Technical validation of a commercial available product
HFO-1234ze*	To be submitted to 57th ExCom	Technical validation of a commercial available product

* A Hydro-Fluoro-Olefin. Full name: trans-1,3,3,3-tetra fluoro propene; $CHF=CHCF_3$

This project covers the validation of methylal in all relevant foam applications. Methylal is a commercially available product that is used mainly for solvent applications and, to a lesser extent, in aerosols. It has no ODP and a negligible GWP. It is in limited use in Europe as a co-blowing agent to enhance HC and HFC systems. However, it has also potential as a sole auxiliary blowing agent in situations where HFCs are not welcomed or HCs are too expensive in investment related to the size of a particular operation. The first is an issue relevant to MOP decision XIX-6 which, under others, stipulates the need to include environmental concerns and the latter is a recurring issue in Article 5 countries where 80% of the enterprises qualify as SME.

Technology validation is a global task. However, it has to be executed in a particular country and UNDP is therefore preparing the proposals in consultation and with the consent of the relevant countries, and requested endorsement letters from the countries are included. However, because of the global impact, deduction of the first phase, which deals with development, optimization and validation from the national aggregate HCFC consumption, would not be fair and it is requested to treat phase-1 this way.

4. INFORMATION ON PARTICIPATING COMPANIES

This pilot project is designed around Arinos Quimica Ltda ("Arinos"), a Brazilian system house. Contact information is as follows:

Company:	Arinos Quimica Ltda
Contact:	Mr. Henrique Bavoso, Commercial Director
Address:	Rua Arinos, 15 – Pq Industrial Agua Vermelha, Osasco, SP CEP 06276-032, Brazil
Ph/Fx/EM:	+5511-3602-7254/+5511-3602-7215/henrique.bavoso@arinos.com.br

Arinos is the successor of Flexquim which was founded in 1993 by Mateos Raduan Dias. The company initially focused on the distribution of chemicals to the flexible PU foam industry. As business evolved into other distribution products and PU systems, it was decided in 1997, along with the relocation to a new, enlarged plant, to rename the business into Arinos because the original name did not match the products anymore. The company is 100 % Brazilian owned. Combined annual sales are US$ 100 million (2008). In addition to its main plant and headquarters in Sao Paulo, it has two branches in the north and the south and three regional sales offices. It employs about 130. Annual sales for the PU system house part have developed as follows (rounded):

2005 US$ 2,300,000 2006 US$ 4,300,000 2007: US$ 7,000,000 2008: US$ 10, 500,000

Arinos has a customer base of about 250 PU companies that purchase systems. Its distribution operation is much larger with 3,500 customers that include non-PU areas such as foodstuff, solvents, pharmaceuticals, etc. From the 250 registered PU system buyers, 50 are regular customers. Arinos also counts with the conditions required to undertake this assignment: knowledge and access to the technology, research and development capacity and interest to undertake the testing.
There is no export to other countries. Base PU chemicals are purchased from Dow, Bayer, Solvay and Momentive (former OSI, the successor of Union Carbide's Silicones Division). The company processes the following auxiliary blowing agents (2007/2008):

Substance	2007	2008	Remarks
HCFC-141b	120 t	180 t	all rigid and integral skin applications
Methylene Chloride	40 t	60 t	packaging foams
Methylal	n/a	n/a	at this time only sample amounts

Methylal is purchased from Lambiotte, Belgium. Lambiotte has developed methylal in Europe as a co-blowing agent in rigid PU foams. Arinos intends to pursue its use as a sole or auxiliary blowing agent as it sees a large potential market in Latin America, which consists in majority of small users that cannot handle pure hydrocarbons and methylal offers the possibility to address flammability issues at the system house only rather than at user level. For this purpose, Arinos has entered into an exclusive distributorship for methylal with Lambiotte. Arinos has preliminary identified 15 companies covering 18 applications that address all major HCFC-consuming PU applications in Brazil.

5. PROJECT DESCRIPTION

The project is divided into two phases:

- Phase-I: development, optimization, validation, technology dissemination
- Phase-II: implementation at recipients covering all applications

5.1 PHASE-I

PU foams are used in applications with different formulations. 18 applications have been identified that use currently HCFC-141b. The first phase, which includes development, optimization and validation of methylal as replacement technology for HCFC-141b will involve the systems house only. Arinos has already developed the technology for one application (packaging foams) but this still will need validation. Phase-I of this project will consist of:

- Acquisition of the necessary testing/prototyping equipment;
- Development of the remaining 17 applications;
- Optimization and validation of all 18 formulations on prototyping equipment;
- Development of safe practices meeting national and international standards for the transportation, storage and use of methylal in system houses and of methylal-containing systems at SMEs;
- Dissemination of the experience gained through a workshop.

Changing blowing agents, essential components in formulations, require determination of baseline values for critical properties. Some, are general in nature but others are specific as the following list shows:

Foam type	Application	Status	Critical Properties	Action
Integral Skin	Steering wheels	Not developed	Friability, surface	Development, Optimization, Validation
	Shoe soles	Not developed	Surface	Development, Optimization, Validation
	Structural (rigid)	Not developed	Surface	Development, Optimization, Validation
	Semi-flexible	Not developed	Surface	Development, Optimization, Validation
Rigid Insulation	Domestic refrigeration	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Commercial refrigeration	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Water heaters	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Trucks	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Panels-continuous	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Panels-discontinuous	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Spray	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Blocks	Not developed	Insulation	Development, Optimization, Validation
	Thermoware	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Pipe-in-pipe	Not developed	Insulation, adhesion	Development, Optimization, Validation
Semi-Rigid	Packaging foam	Developed	Shock absorption	Development, Optimization, Validation
Flexible Foams	Hyper-soft molded	Not developed	Appearance, touch	Development, Optimization, Validation
	Hyper-soft slabstock	Developed	Appearance, touch	Development, Optimization, Validation
	Low resilience	Developed	Resilience curve	Development, Optimization, Validation

Companies and their suppliers do not conduct regular testing on properties of their foams, nor do they set standards. Therefore the acquisition of suitable testing equipment and the determination of baseline data on critical properties is a precondition for a successful validation program. In addition, prototyping equipment is required to limit burdensome and costly downstream production testing to a minimum. The outcome of this part of the project will be a list of application-specific product requirements and tests to measure these. After this, optimization and validation can start in earnest.

Based on the outcome of these programs, the technology will then be technically cleared for industrial application under Phase-II as well for dissemination to other interested system houses world-wide. Past experience has shown how important it is to assure commercial availability and local technical support. In this project, following action is proposed to achieve this goal to the extent possible:

- UNDP has stipulated—and Arinos has agreed to—offering the technology to all system houses in good standing, meeting in this way eligibility criteria (everything that is developed during the project implementation using MLF funds will be public knowledge and will be disclosed).
- Technology dissemination workshops will be conducted for interested systems houses as soon as the technology is deemed transferable.

5.2 PHASE-II

After the formulation for a particular application has successfully passed its evaluation, UNDP will apply for approval of the second project phase, which is application in manufacturing contexts. 15 companies, covering all 18 applications, will apply the technology in their operations. Product and process testing will be conducted by the system house. UNDP will conduct safety audits. Process adaptations will be made as needed to meet requirements as indicated in the previous table. This phase is not part of the present submission, which is focused in validation of the technology.

5.3 SUPERVISION ARRANGEMENTS

Decision 55/43 requires Agencies to report accurate project cost data as well as other data relevant to the application of the technologies through *"a progress report after each of the two implementation phases"*. UNDP suggests in addition supervision of the validation by the UNEP Foams Technical Options Committee. The FTOC has, in its September 2008 meeting, in principle agreed to such an assignment.

6. TECHNICAL OPTIONS FOR HCFC REPLACEMENT IN PU FOAMS

6.1 GENERAL OVERVIEW

Annex-1 provides an overview of all HCFC-141b replacement technologies that are currently available, proposed or under development. Based on these data, it appears that

- Straight conversion of HCFCs to HFCs will always increase the GWP;
- HCs, CO_2 (liquefied or derived from water), methylal and methyl formate will be options in PU foams that decrease—virtually eliminate—GWP in PU foams;
- Emerging technologies such as HBA-2, AFA-L1 and FEA 1100 will require at least two more years before (potential) commercialization;
- PU validation may therefore include cost-optimized hydrocarbons, methyl formate, methylal and environmentally optimized HFC formulations.

6.2 METHYLAL AS REPLACEMENT TECHNOLOGY FOR HCFC-141b

Methylal, also called dimethoxymethane, belongs to the acetyl family. It is a clear colorless, chloroform-like odor, flammable liquid with a relatively low boiling point. Its primary uses are as a solvent and in the manufacture of perfumes, resins, adhesives, paint strippers and protective coatings. It is soluble in three parts water and miscible with the most common organic solvents.

Property	**Methylal**	**HCFC-141b**
Appearance	Clear liquid	Clear liquid
Boiling point	42 °C	32 °C
LEL/UEL	2.2-19.9 %	7.6-17.7
Vapor pressure	400 mm Hg @ 20 °C	593 mm Hg @ 25 °C
Lambda, gas	14.5 mW/m.k@ 42 °C	10.0 mW/m.k @ 25 °C
Auto ignition	235 °C	>200 °C
Specific gravity	0.821 @ 20 °C	1.24
Molecular weight	76.09	117
GWP	Negligible	630
TLV (USA)	1000 ppm TWA	500 ppm TWA/500 ppm STEL

Methylal has a very low toxicity while HCFC-141b classifies as moderately toxic:

	Methylal	**HCFC-141b**
• TLV (MAK):	1000 ppm	500 ppm
• Acute toxicity:	LD50 > 7 g/kg	8,000 ppm
• Acute inhalation toxicity (LC50)	15,000 ppm	10,000 ppm
• LC50	18,354 ppm	92,000 ppm
• Sub-acute inhalation	NOEL = 4,000 ppm (8 x 6 h)	20,000 ppm
• Sub-chronic inhalation:	NOEL = 2,000 ppm	20,000 ppm
• Eye irritation:	minor to moderate	minor to moderate
• Skin irritation:	none to slight	none to slight
• Dermal sensitization:	not allergenic	non allergenic
• Ames test:	no mutagenic activity	no mutagenic activity

Methylal has also lower eco-toxicity than HCFC 141b:

	Methylal	**HCFC-141b**
• Daphnids, fish (Brachydanio Rerio)	no effect	31.2 – 126 mg/L
• Biodegradability (ISO/DIS 8192)	biodegradable	not biodegradable

Methylal is, however flammable:

- flash point (open cup): -18°C (-0.4°F)
- auto-ignition temperature: 237°C (458.6°F)
- explosion limits: 1.6 % vol (LEL)/17.6 % vol (UEL)

Methylal as proposed, however, will reduce—or even eliminate—the related risk by premixing at the system house. Consequently, safety precautions will be less than for current HC applications.

Following is a list comparing methylal with other, common foam blowing agents on the most relevant properties:

	HCFC-141b	**Methylal**	**Cyclo Pentane**	**HFC-245fa**
LEL/UEL (%)	7.3-16.0	1.6/17.6	1.4-8.0	none
Molecular Weight	117	76	70	134
Gas Conductivity (mW/m°K)	10 (25°C)	14.5 (42°C)*	11 (10°C)	12.5 (24°C)
TLV/OEL (ppm)	500 (TLV)	1,000 (TLV)	600 (TLV)	300 (WHEEL)
GWP (100 y; IPCC-1996)	630	Negligible	11	820
ODP	0.11	0	0	0

*Extrapolation at 25 °C would be ~ 11

In summary, methylal compares very well to other, commercially available, HCFC replacement alternatives. UNDP's conclusion is that the chemical is worth a thorough validation.

Apart from the use of methylal as sole auxiliary blowing agent, its use as a co-blowing agent in conjunction with hydrocarbons and HFCs for rigid foam applications has been described in the literature. It is claimed that in continuous panels methylal improves the miscibility of pentane, promotes blending in the mixing head, foam uniformity, flow, adhesion to metal surfaces and insulation properties, reducing simultaneously the size of the cells. In discontinuous panels, where most producers use non-flammable agents, the addition of a low percentage of Methylal to HFCs (245fa, 365mfc or 134a) makes it possible to prepare pre-blends with polyols of low flammability with no detrimental effect on the fire performance of the foam. Methylal reduces the cost, improves the miscibility, the foam uniformity and flow and the adhesion to metal surfaces. Co-blown with HFC-365mfc, it also improves the thermal insulation. In domestic refrigeration compared to cyclopentane alone Methylal increases blowing rate and compressive strength. In sprayfoam it reduces the cost of HFC-245fa/-365mfc. There is no known use of methylal as sole auxiliary blowing agent.

Finally, it would be interesting to apply methylal in natural polyol systems—such as castor or soy oil based polyols. Such systems have generated high interest in Brazil and world-wide.

Despite all literature references, public knowledge of methylal's industrial performance as blowing agent is quite limited. To validate its use as a possible replacement of HCFCs for MLF projects in developing countries, peer reviewed evaluations should be carried out to assess its performance in integral skin and rigid insulating foams. Following parameters should be carefully monitored:

- Fire performance in actual operating conditions (considering flammability of the pure chemical)
- Polyol miscibility, an advantage claimed in the literature
- Foam flow (taking into account the relatively high -compared to other blowing agents- boiling point)
- Foam thermal conductivity (Gas conductivity value is not reported)
- Skin formation. (A cited US patent suggests a clear benefit)
- Diffusion rate in the polyurethane matrix (in view of its high solvent power)

One could ask if future use of methylal in an additional application—foams—would not stress the supply and therefore would have price implications. However, the potential use in foams is just a fraction of the current use in other applications and no supply issue is therefore expected. Methylal is offered in different purities. It is recommended that the pure grade suits its use as blowing agent best:

Compound	Cosmetic Grade	Anhydrous Grade	Pure Grade	Technical Grade
Methylal	**99.5 % min.**	**99.9 % min.**	**99.5 % min.**	**93 % min.**
Methanol	< 1 ppm	< 0.05 %	< 0.05 %	6.5 % max
Formaldehyde	< 1 ppm	< 0.005 %	< 0.0005 %	< 0.02 %
Water	< 0.5 %	< 0.03 %	< 0.5 %	< 0.25 %

7. PROJECT COSTS

Making cost forecasts for pilot projects is difficult as they are by nature unpredictable. UNDP has used to the extent possible guidance provided by the Secretariat in Doc 55/47 Annex III, Appendix II. One uncertainty is the flammability. The Material Safety Data Sheet (MSDS) mentions methylal to be "highly flammable". On the other side, it can be expected that emissions from PU systems containing methylal and from the actual foam process will be much lower—likely even below applicable explosion limits. UNDP considers the process at the system house (prototyping, blending) hazardous and requiring adequate safeguards but the use of pre-blended systems may be non-flammable. That implies that from the 18 applications most likely only 3 (all continuous operations that directly meter the blowing agent) are deemed to require safeguards. Consequently, the Secretariat's template for flammable blowing agents has been used in 4 cases (three users and the system house) and the template for non-flammable substances 12 cases. This has a beneficial impact on the expected budget. The price of methylal in Brazil is US$ 3.00/kg while HCFC-141b is US$ 2.40. However, the molecular weight of methylal is lower so that a better blowing efficiency can be expected. This may be partially offset by solubility and diffusion so that an actual prediction is difficult and the calculation of IOCs should await the results of the system development. Following are the summarized cost expectations:

#	ACTIVITY	COSTS (US$)		
		INDIVIDUAL	SUB-TOTAL	TOTAL
	PHASE-I – DEVELOPMENT/OPTIMIZATION/VALIDATION/DISSEMINATION			
1	Preparative work Project Preparation Technology Transfer, Training	 30,000 25,000	55,000	**464,200**
2	System Preparation Development (17 applications) @ 5,000 Optimization (17 applications) @ 3,000 Validation (18 applications) @ 2,000	 85,000 51,000 36,000	172,000	
3	Laboratory Equipment K-factor tester US$ 10,000 Refractometer 5,000 Brett mold 5,000 HP laboratory dispenser 50,000 Sprayfoam/PIP dispenser 20,000 pH tester 5,000 Abrasion tester 25,000 Cell gas analyzer 20,000 Laboratory Safety	 10,000 5,000 5,000 50,000 20,000 5,000 25,000 20,000 10,000	150,000	
4	Peer review/preparation of next phase		20,000	
5	Technology Dissemination Workshops		25,000	
6	Contingencies (10%)		42,200	

	PHASE-II – HCFC PILOT PHASEOUT PROJECT COVERING ALL APPLICATIONS (tentative and not part of the current funding request)			
1	System House adaptations 1 Blender 1 Tank for Methylal Safety measures Contingencies (10%)	 50,000 20,000 25,000 9,500	104,500	**629,700 + IOCs**
2	Discontinuous Operations (12) 14 Retrofits @ 15,000 14 Trial Programs @ 3,000 Contingencies (10%)	 210,000 42,000 25,200	277,200	
3	Continuous Operations (3) 3 ex proof metering systems @ 15,000 3 ventilation units @ 25,000 3 sensor systems @ 15,000 3 grounding programs @ 5,000 Contingencies	 45,000 75,000 45,000 15,000 18,000	198,000	
4	Peer review/safety audits		50,000	
5	Incremental Operating Costs		Not determined	

UNDP requests at this stage a grant for the first phase of this project amounting to **US$ 464,200.**

8. IMPLEMENTATION/MONITORING

TASKS	2009				2010			
	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q
Project Start-up								
MF Project Approval	X							
Receipt of Funds		X						
Grant Signature		X						
Management activities								
-Monitoring/oversight activities in place		X						
-Progress Reports to NOU and Excom			X		X	X	X	

Phase-I								
-Procurement		X						
-Installation			X					
-System development		XX	X					
-System optimization		X	XX					
-System validation at system house			XXX					
-Peer review/detailed design of phase- II			X					
-Approval phase-II				X				
- Technology Dissemination Workshop(s)				X				

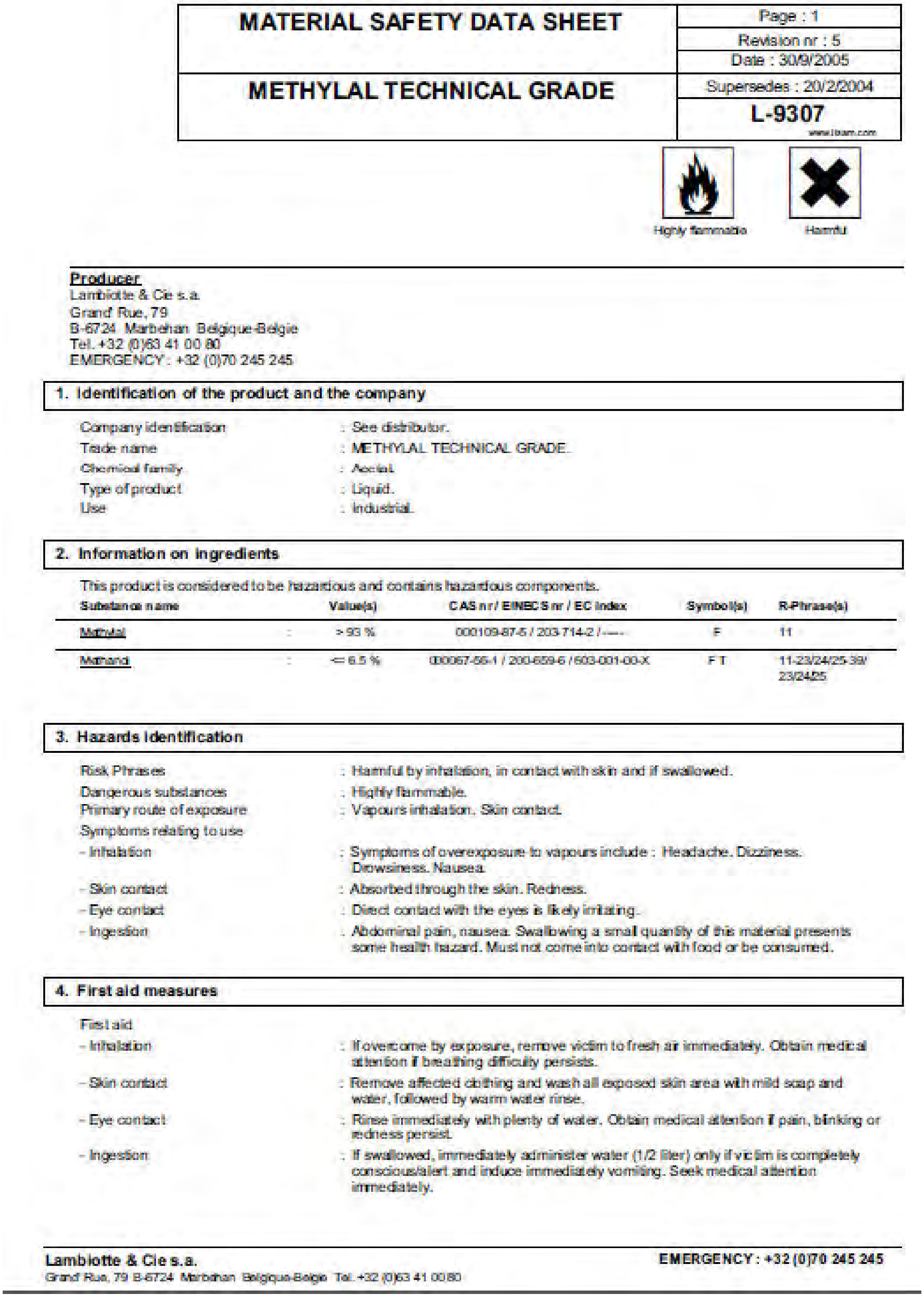
Phase-II								
-Prepare individual Implementation plans				X				
-Procurement					X			
-Installation/start-up						XX		
-Trials						XX		
-Certificates of Technical Completion (COCs)						XX		
-Handover Protocols (HOPs)						X	X	
-Completion Report (PCR)							X	

MILESTONES FOR PROJECT MONITORING

TASK	MONTH*
(a) Project document submitted to beneficiaries	2
(b) Project document signatures	3
(c) Bids prepared and requested	3, 9
(d) Contracts Awarded	3, 9
(e) Equipment Delivered	4, 11
(f) Training Testing and Trial Runs	4, 12
(g) Commissioning (COC)	14
(h) HOP signatures	15
(1) Compliance Monitoring	17

* As measured from project approval

ATTACHMENT II:
MATERIAL SAFETY DATA SHEET/OSHA GUIDELINES



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METHYLAL TECHNICAL GRADE	Supersedes : 20/2/2004
	L-9307 www.lisam.com

Highly flammable

Harmful

Producer
Lambiotte & Cie s.a.
Grand' Rue, 79
B-6724 Marbehan Belgique-Belgie
Tel. +32 (0)63 41 00 80
EMERGENCY : +32 (0)70 245 245

1. Identification of the product and the company

Company identification : See distributor.
Trade name : METHYLAL TECHNICAL GRADE.
Chemical family : Acetal.
Type of product : Liquid.
Use : Industrial.

2. Information on ingredients

This product is considered to be hazardous and contains hazardous components.

Substance name		Value(s)	CAS nr / EINECS nr / EC index	Symbol(s)	R-Phrase(s)
Methylal	:	> 93 %	000109-87-5 / 203-714-2 / -----	F	11
Methanol	:	<= 6.5 %	000067-56-1 / 200-659-6 / 603-001-00-X	F T	11-23/24/25-39/ 23/24/25

3. Hazards identification

Risk Phrases : Harmful by inhalation, in contact with skin and if swallowed.
Dangerous substances : Highly flammable.
Primary route of exposure : Vapours inhalation. Skin contact.
Symptoms relating to use
- Inhalation : Symptoms of overexposure to vapours include : Headache. Dizziness. Drowsiness. Nausea.
- Skin contact : Absorbed through the skin. Redness.
- Eye contact : Direct contact with the eyes is likely irritating.
- Ingestion : Abdominal pain, nausea. Swallowing a small quantity of this material presents some health hazard. Must not come into contact with food or be consumed.

4. First aid measures

First aid
- Inhalation : If overcome by exposure, remove victim to fresh air immediately. Obtain medical attention if breathing difficulty persists.
- Skin contact : Remove affected clothing and wash all exposed skin area with mild soap and water, followed by warm water rinse.
- Eye contact : Rinse immediately with plenty of water. Obtain medical attention if pain, blinking or redness persist.
- Ingestion : If swallowed, immediately administer water (1/2 liter) only if victim is completely conscious/alert and induce immediately vomiting. Seek medical attention immediately.

Lambiotte & Cie s.a.
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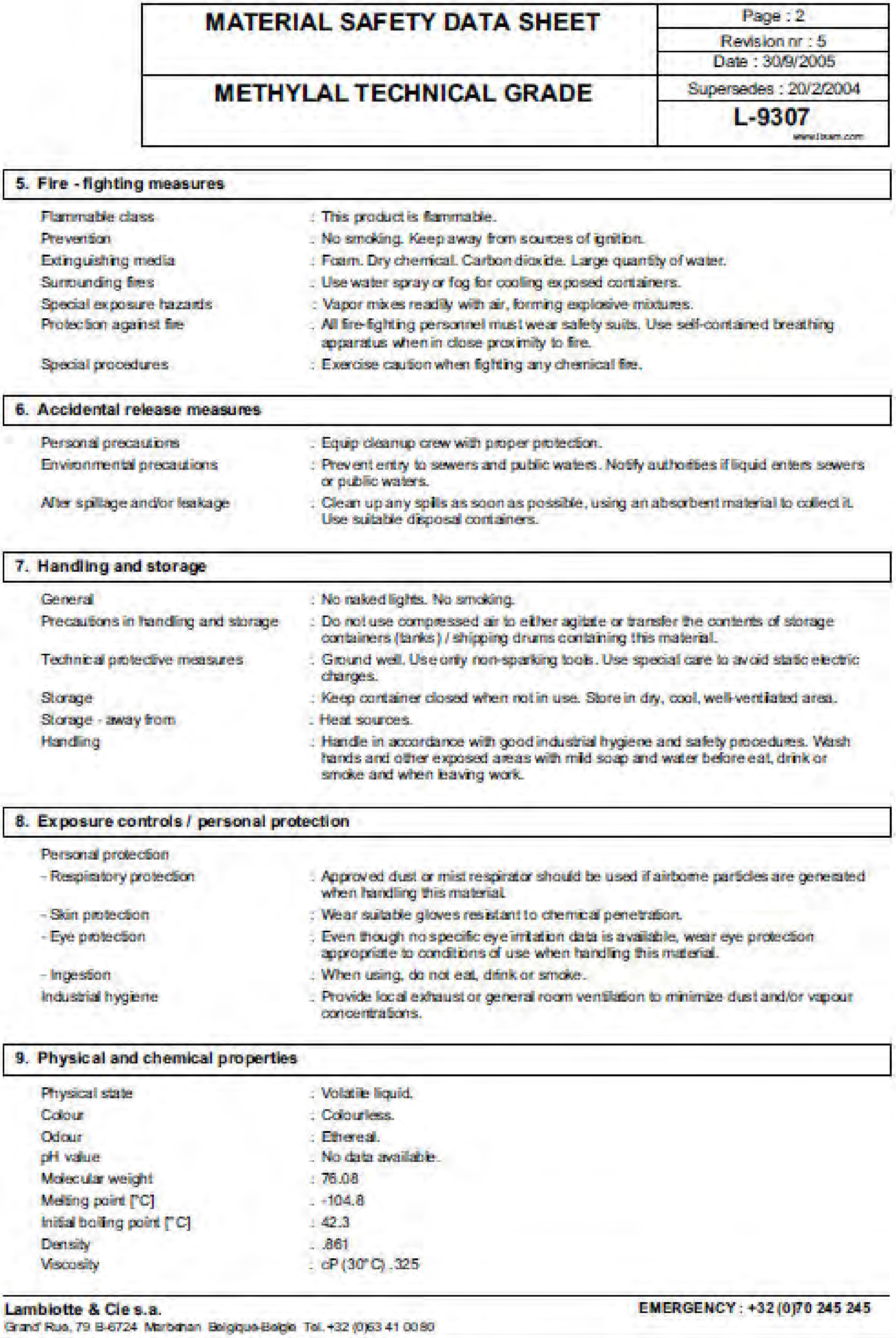

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5. Fire - fighting measures

Flammable class	: This product is flammable.
Prevention	: No smoking. Keep away from sources of ignition.
Extinguishing media	: Foam. Dry chemical. Carbon dioxide. Large quantity of water.
Surrounding fires	: Use water spray or fog for cooling exposed containers.
Special exposure hazards	: Vapor mixes readily with air, forming explosive mixtures.
Protection against fire	: All fire-fighting personnel must wear safety suits. Use self-contained breathing apparatus when in close proximity to fire.
Special procedures	: Exercise caution when fighting any chemical fire.

6. Accidental release measures

Personal precautions	: Equip cleanup crew with proper protection.
Environmental precautions	: Prevent entry to sewers and public waters. Notify authorities if liquid enters sewers or public waters.
After spillage and/or leakage	: Clean up any spills as soon as possible, using an absorbent material to collect it. Use suitable disposal containers.

7. Handling and storage

General	: No naked lights. No smoking.
Precautions in handling and storage	: Do not use compressed air to either agitate or transfer the contents of storage containers (tanks) / shipping drums containing this material.
Technical protective measures	: Ground well. Use only non-sparking tools. Use special care to avoid static electric charges.
Storage	: Keep container closed when not in use. Store in dry, cool, well-ventilated area.
Storage - away from	: Heat sources.
Handling	: Handle in accordance with good industrial hygiene and safety procedures. Wash hands and other exposed areas with mild soap and water before eat, drink or smoke and when leaving work.

8. Exposure controls / personal protection

Personal protection	
- Respiratory protection	: Approved dust or mist respirator should be used if airborne particles are generated when handling this material.
- Skin protection	: Wear suitable gloves resistant to chemical penetration.
- Eye protection	: Even though no specific eye irritation data is available, wear eye protection appropriate to conditions of use when handling this material.
- Ingestion	: When using, do not eat, drink or smoke.
Industrial hygiene	: Provide local exhaust or general room ventilation to minimize dust and/or vapour concentrations.

9. Physical and chemical properties

Physical state	: Volatile liquid.
Colour	: Colourless.
Odour	: Ethereal.
pH value	: No data available.
Molecular weight	: 76.08
Melting point [°C]	: -104.8
Initial boiling point [°C]	: 42.3
Density	: .861
Viscosity	: cP (30°C) .325

Lambiotte & Cie s.a.
Grand' Rue, 79 B-6724 Marbehan Belgique-Belgie Tel. +32 (0)63 41 00 80

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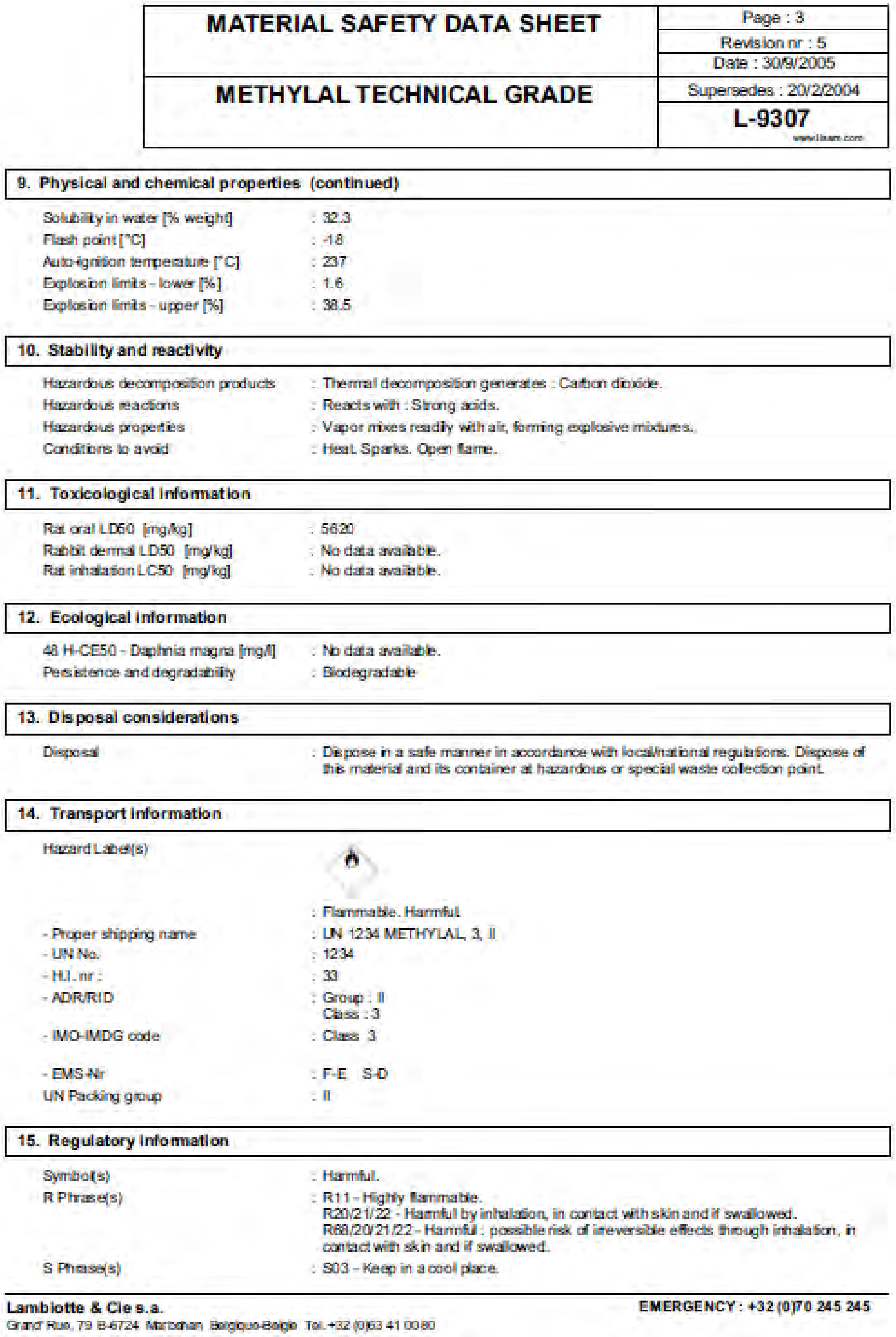

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9. Physical and chemical properties (continued)

Solubility in water [% weight]	: 32.3
Flash point [°C]	: -18
Auto-ignition temperature [°C]	: 237
Explosion limits - lower [%]	: 1.6
Explosion limits - upper [%]	: 38.5

10. Stability and reactivity

Hazardous decomposition products	: Thermal decomposition generates : Carbon dioxide.
Hazardous reactions	: Reacts with : Strong acids.
Hazardous properties	: Vapor mixes readily with air, forming explosive mixtures.
Conditions to avoid	: Heat. Sparks. Open flame.

11. Toxicological information

Rat oral LD50 [mg/kg]	: 5620
Rabbit dermal LD50 [mg/kg]	: No data available.
Rat inhalation LC50 [mg/kg]	: No data available.

12. Ecological information

48 H-CE50 - Daphnia magna [mg/l]	: No data available.
Persistence and degradability	: Biodegradable

13. Disposal considerations

Disposal	: Dispose in a safe manner in accordance with local/national regulations. Dispose of this material and its container at hazardous or special waste collection point.

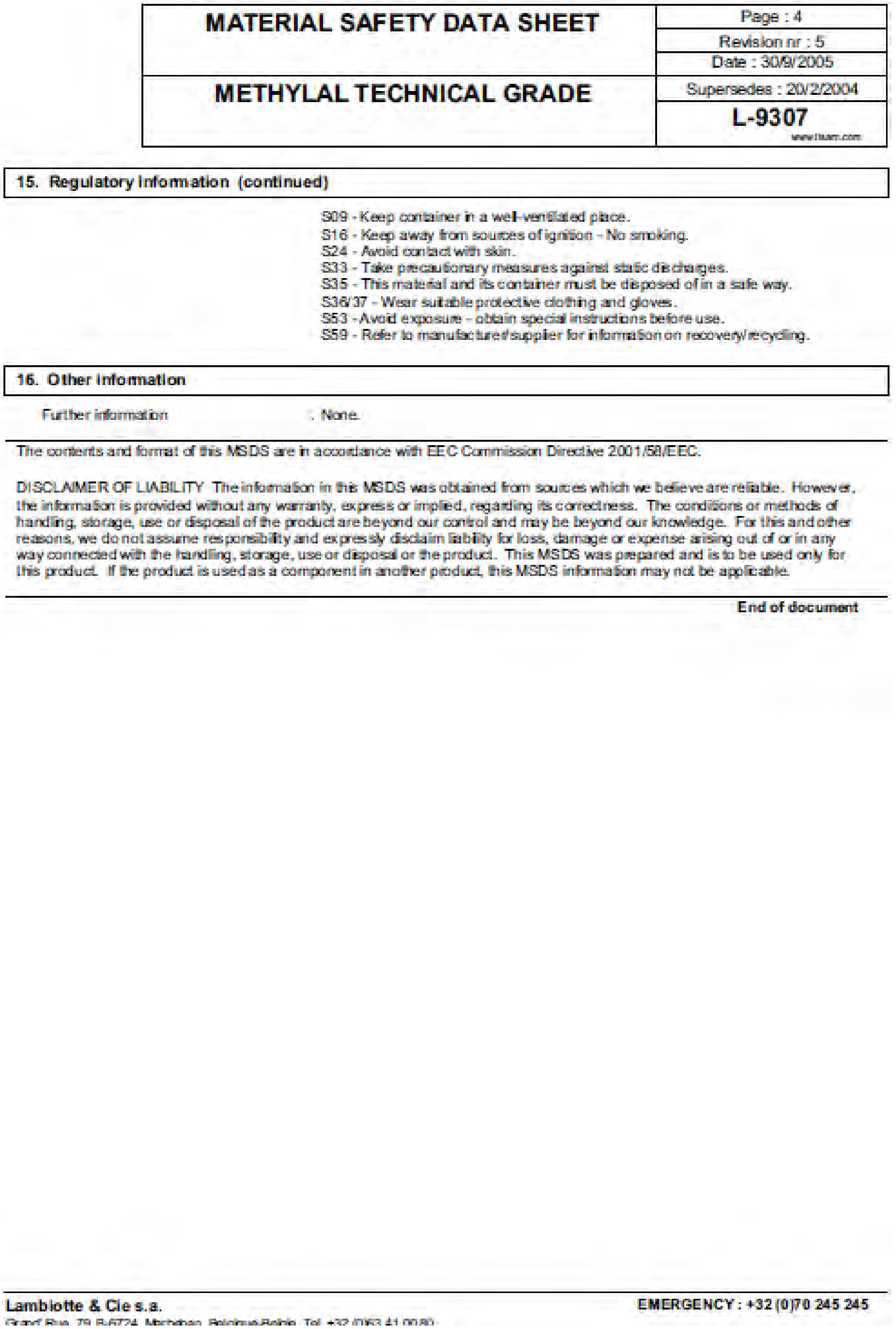
14. Transport information

Hazard Label(s)	: Flammable. Harmful.
- Proper shipping name	: UN 1234 METHYLAL, 3, II
- UN No.	: 1234
- H.I. nr :	: 33
- ADR/RID	: Group : II Class : 3
- IMO-IMDG code	: Class 3
- EMS-Nr	: F-E S-D
UN Packing group	: II

15. Regulatory information

Symbol(s)	: Harmful.
R Phrase(s)	: R11 - Highly flammable. R20/21/22 - Harmful by inhalation, in contact with skin and if swallowed. R68/20/21/22 - Harmful : possible risk of irreversible effects through inhalation, in contact with skin and if swallowed.
S Phrase(s)	: S03 - Keep in a cool place.

Lambiotte & Cie s.a. **EMERGENCY : +32 (0)70 245 245**
Grand' Rue, 79 B-6724 Marbehan Belgique-België Tel. +32 (0)63 41 00 80



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15. Regulatory Information (continued)

S09 - Keep container in a well-ventilated place.
S16 - Keep away from sources of ignition - No smoking.
S24 - Avoid contact with skin.
S33 - Take precautionary measures against static discharges.
S35 - This material and its container must be disposed of in a safe way.
S36/37 - Wear suitable protective clothing and gloves.
S53 - Avoid exposure - obtain special instructions before use.
S59 - Refer to manufacturer/supplier for information on recovery/recycling.

16. Other information

Further information : None.

The contents and format of this MSDS are in accordance with EEC Commission Directive 2001/58/EEC.

DISCLAIMER OF LIABILITY The information in this MSDS was obtained from sources which we believe are reliable. However, the information is provided without any warranty, express or implied, regarding its correctness. The conditions or methods of handling, storage, use or disposal of the product are beyond our control and may be beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal or the product. This MSDS was prepared and is to be used only for this product. If the product is used as a component in another product, this MSDS information may not be applicable.

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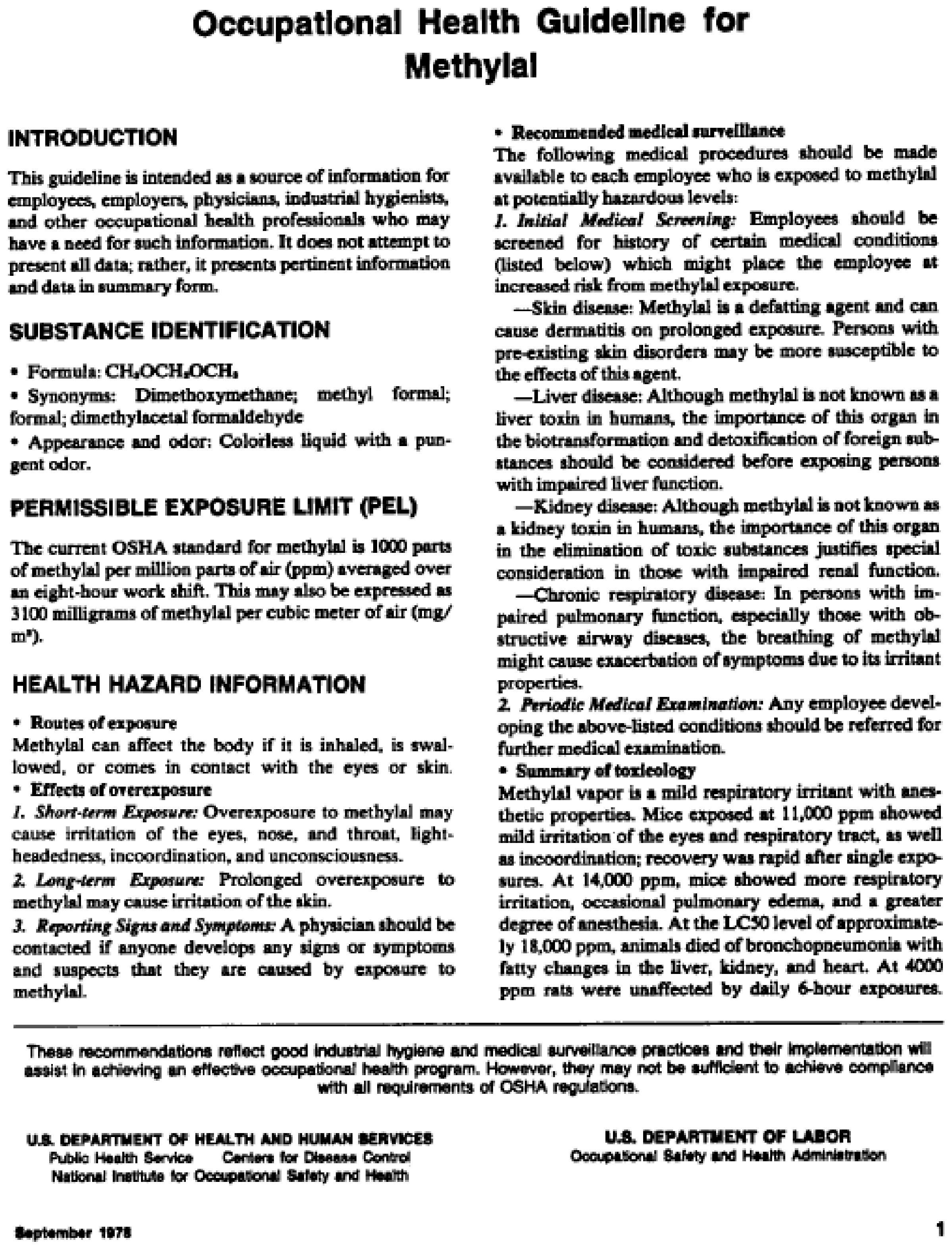
Grand' Rue, 79 B-6724 Marbehan, Belgique-België, Tel. +32 (0)63 41 00 80



Occupational Health Guideline for Methylal

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3OCH_2OCH_3$
- Synonyms: Dimethoxymethane; methyl formal; formal; dimethylacetal formaldehyde
- Appearance and odor: Colorless liquid with a pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylal is 1000 parts of methylal per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3100 milligrams of methylal per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylal can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methylal may cause irritation of the eyes, nose, and throat, lightheadedness, incoordination, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure to methylal may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylal.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylal at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylal exposure.

—Skin disease: Methylal is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methylal is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methylal is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylal might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylal vapor is a mild respiratory irritant with anesthetic properties. Mice exposed at 11,000 ppm showed mild irritation of the eyes and respiratory tract, as well as incoordination; recovery was rapid after single exposures. At 14,000 ppm, mice showed more respiratory irritation, occasional pulmonary edema, and a greater degree of anesthesia. At the LC50 level of approximately 18,000 ppm, animals died of bronchopneumonia with fatty changes in the liver, kidney, and heart. At 4000 ppm rats were unaffected by daily 6-hour exposures.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

Skin irritation may be expected due to defatting action by the solvent, and eye irritation if splashing occurs. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76
2. Boiling point (760 mm Hg): 44 C (111 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of methylal): 2.6
5. Melting point: −105 C (−157 F)
6. Vapor pressure at 20 C (68 F): 330 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 33
8. Evaporation rate (butyl acetate = 1): 23.1

- **Reactivity**

1. Conditions contributing to instability: Heat, presence of acids
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde, and methyl alcohol) may be released in a fire involving methylal.
4. Special precautions: Methylal will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −18 C (−4 F) (closed cup)
2. Autoignition temperature: 237 C (459 F)
3. Flammable limits in air, % by volume: Lower: 1.6; Upper: 17.6
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold, but Browning notes that it has a slightly pungent odor.
2. Eye Irritation Level: Grant states that "exposures of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially were found to cause . . . occasional irritation of the eyes but no histologically demonstrable abnormality of the optic nerve or retina."

Patty reports that mice which had received 15 7-hour exposures at 11,000 ppm experienced only mild irritation.

No quantitative information is available, however, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Since there is no useful quantitative information relating warning properties to air concentrations of methylal, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

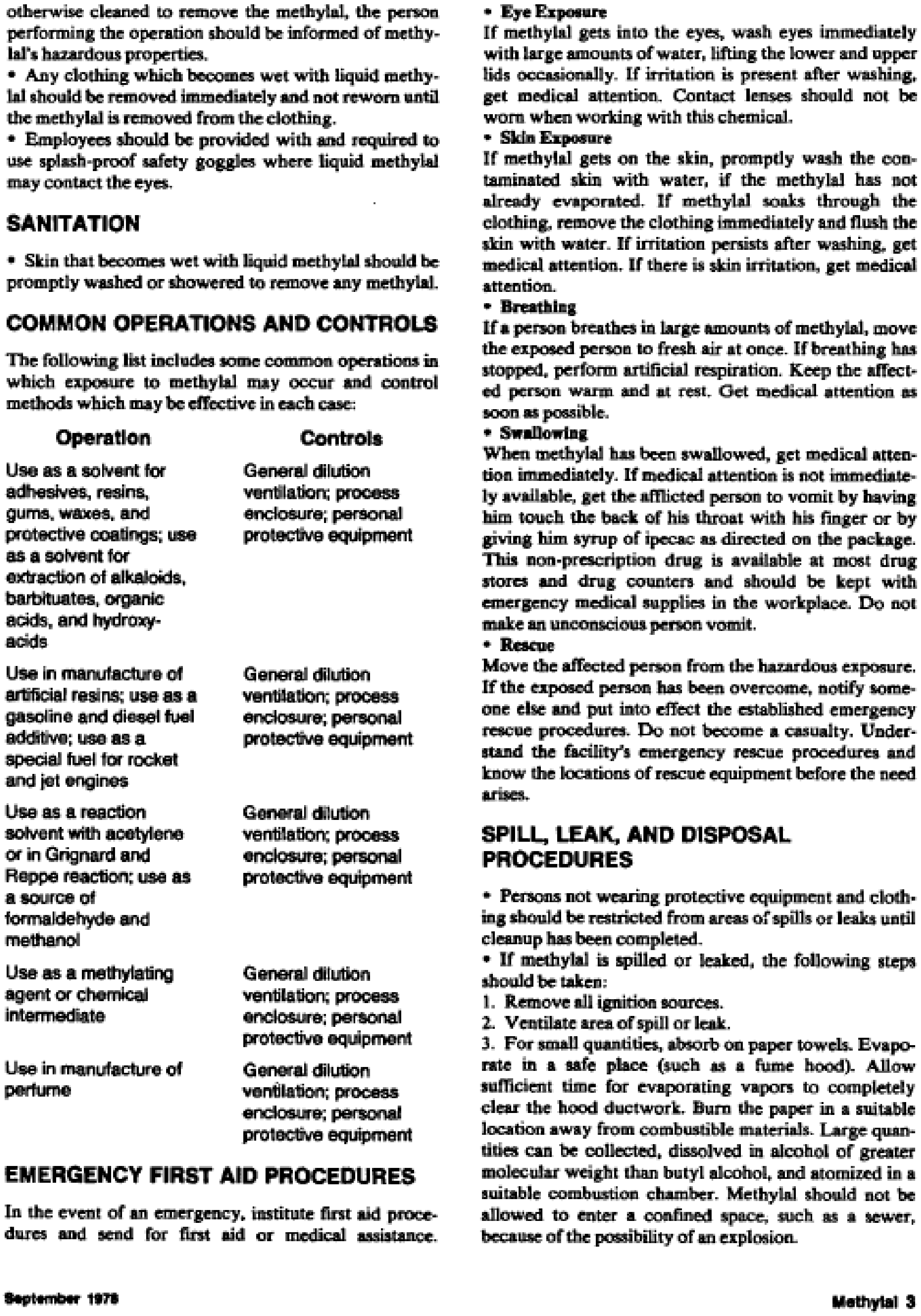
Sampling and analyses may be performed by collection of methylal vapors using an adsorption tube with subsequent desorption with hexane and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylal may be used. An analytical method for methylal is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylal.
- Clothing wet with liquid methylal should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylal from the clothing. If the clothing is to be laundered or



otherwise cleaned to remove the methylal, the person performing the operation should be informed of methylal's hazardous properties.

- Any clothing which becomes wet with liquid methylal should be removed immediately and not reworn until the methylal is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylal may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methylal should be promptly washed or showered to remove any methylal.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylal may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent for adhesives, resins, gums, waxes, and protective coatings; use as a solvent for extraction of alkaloids, barbituates, organic acids, and hydroxy-acids	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of artificial resins; use as a gasoline and diesel fuel additive; use as a special fuel for rocket and jet engines	General dilution ventilation; process enclosure; personal protective equipment
Use as a reaction solvent with acetylene or in Grignard and Reppe reaction; use as a source of formaldehyde and methanol	General dilution ventilation; process enclosure; personal protective equipment
Use as a methylating agent or chemical intermediate	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of perfume	General dilution ventilation; process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methylal gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methylal gets on the skin, promptly wash the contaminated skin with water, if the methylal has not already evaporated. If methylal soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methylal, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methylal has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methylal is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Methylal should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Methylal may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

REFERENCES

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- Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.
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- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Weaver, F. L., et al.: "Toxicity of Methylal," *British Journal of Industrial Medicine*, 8:279-283, 1951.

RESPIRATORY PROTECTION FOR METHYLAL

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

ATTACHMENT III:
PROCESS EMISSIONS

ATTACHMENT IV
TOXICOLOGICAL PROFILE

Lambiotte & Cie S.A.

METHYLAL

(DIMETHOXYMETHANE)

TOXICOLOGICAL PROFILE

18, avenue des Aubépines
B - 1180 Brussels
BELGIUM
Tel. : +32-2-374 44 65
Fax : +32-2-375 31 55

October 19th, 1998

ACUTE TOXICITY STUDIES

Ref #	Species/ strain	Initial Group	Route of administration	Dose mg/kg bw*	Dilution	Document ID	LD 50 mg/kg bw *	Comments	Date	Laboratory
1	Mouse NA	NA	Oral (gavage ?)	NA	Undiluted	1	6,950	NA	May 1983	Municipal Public Health Department, Moscow USSR
2	Rat NA	NA	Oral (gavage ?)	NA	Undiluted	1	9,070	NA	May 1983	Municipal Public Health Department, Moscow USSR
3	Rat NA	Total : 8 F 2 F per dose	Oral (gavage ?)	1,000 2,000 3,980 7,950	Undiluted	2	> 7,950	No mortality up to 7,950 mg/kg	Dec. 1968	Dow Chemical Company USA
4	Rat Wistar	Total : 50 5 M + 5 F per dose	Oral (gavage)	1 ml/kg bw 2 « » 4 « » 8 « » 16 « »	Undiluted	3	7.46 ml/kg bw = 6.415 mg/kg bw	No mortality up to 4 ml/kg bw. Sluggishness at all doses No gross pathology changes up to 8 (males) or 2 (females) ml/kg bw	Dec. 1982	Bushy Run Research Center, PA USA
5	Rabbit NA	NA	Oral (gavage)	4560 5700	Diluted in water	4	5,700	Mortality : 1/5 at 4560 mg/kg bw 4/7 at 5700 mg/kg bw	1932	University of California Medical School, San Francisco USA

*** Unless otherwise stated**
NA : Information not available

ACUTE TOXICITY STUDIES (continued)

Ref #	Species/ strain	Initial Group	Route of administration	Dose mg/kg bw*	Dilution	Document ID	LD 50 mg/kg bw *	Comments	Date	Laboratory
6	Rabbit New Zealand	Total : 10 5 M + 5 F	Topical covered for 24 h	5,000	Undiluted	5	> 5,000	No mortality No treatment related clinical signs nor gross pathology changes	Nov. 1989	Springborn Laboratories, Ohio **USA**
7	Rabbit New Zealand	Total : 20 10 M + 10 F	Topical covered for 24 h	- 1 ml/kg bw (4 M + 4 F) - 4 ml/kg bw (2 M + 2 F) -16ml/kg bw (4 M + 4 F)	Undiluted	3	> 16 ml/kg bw = 13,760 mg/kg bw	No mortality. Clinical signs at 4 and 16 ml/kg bw Local irritation at 16ml/kg bw Gross pathology changes at 1 and 16 ml/kg bw	Dec. 1982	Bushy Run Research Center, PA **USA**
8	Mouse ICR	Total : 30 3 M + 3 F per dose	Intraperitoneal	500 1,625 2,750 3,875 5,000	Diluted with 0.9% aqueous sodium chloride	6	> 3,875 < 5,000	Mortality 5 out of 6 mice at 5,000 mg/kg bw Clinical signs at 2,750 and above	June 1990	Hazleton Laboratories, MD **USA**
9	Guinea Pig NA	NA	Subcutaneous	3.0 ml/kg bw 3.5 5.0	NA	7	> 5 ml/kg bw = 4,300 mg/kg bw	No mortality up to 5 ml/kg bw Local reaction at injection sites	1951	NIH **USA**
10	Mouse Swiss	(?) groups of 10 animals	Inhalation	NA 7 h exposure		7	LC 50 = 18,354 ppm	Nervous signs preceeding death	1951	NIH **USA**

*** Unless otherwise stated**
NA : Information not available

ACUTE TOXICITY STUDIES (continued)

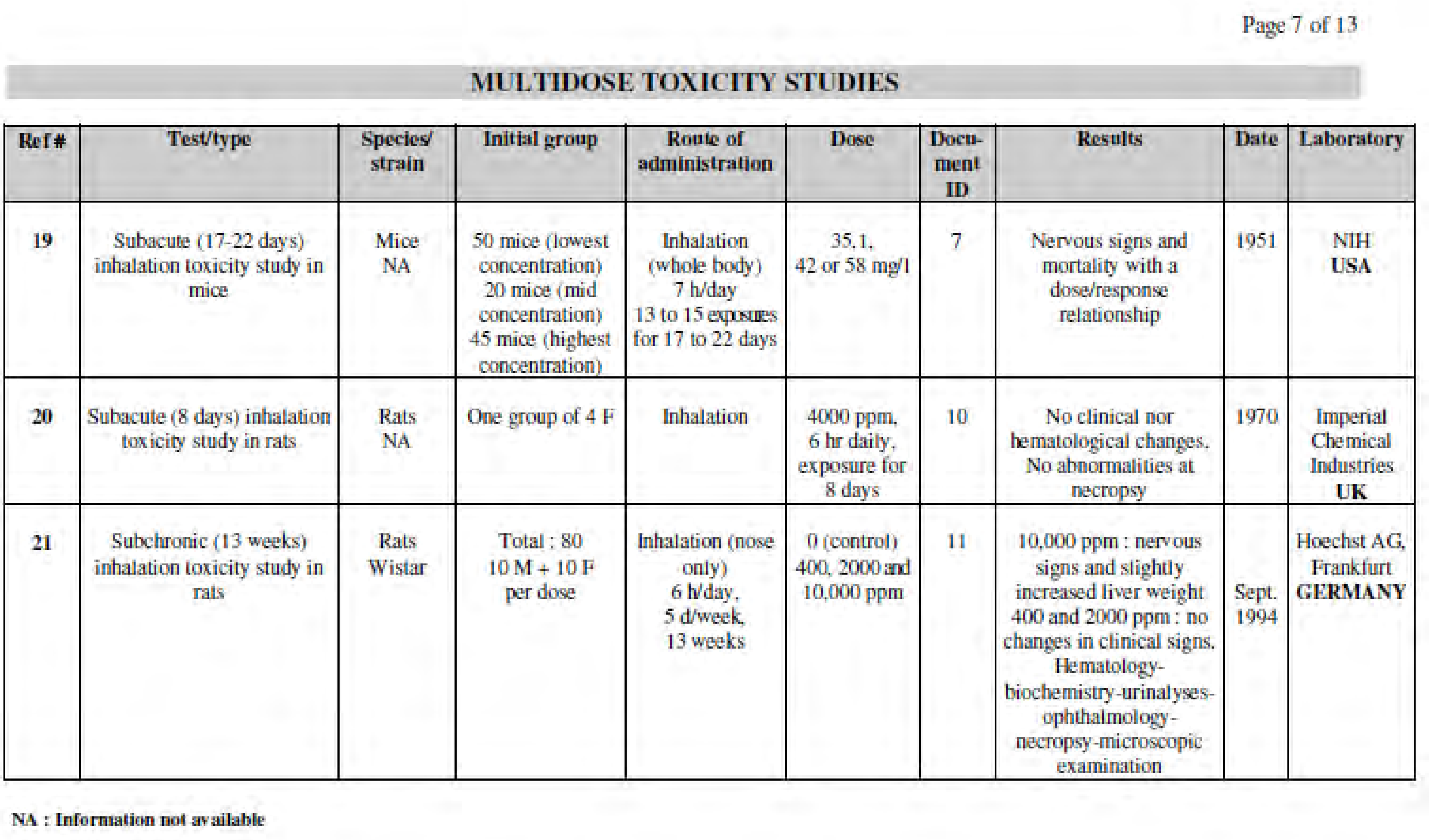
Ref #	Species/ strain	Initial Group	Route of administration	Dose mg/kg bw*	Dilution	Document ID	LD 50 mg/kg bw *	Comments	Date	laboratory
11	Rat NA	NA	Inhalation	NA		8	LC 50 = 15,000 ppm	NA	NA	NA
12	Rat Wistar	Total : 30 5 M + 5 F per dose	Inhalation	Saturated vapor 23° C Exposure for 14, 27 or 51 min (males) or 18, 35 or 64 min (females)		3	NA	Death occurred between 14 to 27 min (males) or 18 to 35 min (females) Nervous signs observed	Dec. 1982	Bushy Run Research Center, PA **USA**
13	Guinea Pig NA	NA	Inhalation	NA		7	NA	Clinical signs and deaths at concentrations around 150,000 ppm in one and a half to two and a half hours.	1951	NIH **USA**

*** Unless otherwise stated**
NA : Information not available

LOCAL TOLERANCE STUDIES

Ref #	Species/ Strain	Initial group	Route of administration	Number of applications	Dilution/dose	Document ID	Comments	Date	Laboratory
14	Rabbit NA	NA	Topical (ocular instillation)	1	Undiluted	2	Unwashed : moderate to severe conjonctival irritation washed : moderate conjonctival irritation	Dec. 1968	Dow Chemical Company USA
15	Rabbit New Zealand	Total : 12 6 females per dose	Topical (ocular instillation)	1	Undiluted 0.01 ml/eye 0.1 ml/eye	3	0.01 ml : minor irritation of conjunctivae 0.1 ml : minor corneal and iridal injury. Minor to moderate conjunctival irritation	Dec. 1982	Bushy Run Research Center, PA USA
16	Rabbit New Zealand	Total : 6 3 M + 3 F	Topical	1	Undiluted 0.5 ml 4 hour exposure	3	No cutaneous reaction	Dec. 1982	Bushy Run Research Center, PA USA
17	Rabbit New Zealand	Total : 6 2 M + 4 F	Topical	1	Undiluted 0.5 ml 4 hour period	9	Slight transient erythema Primary irritation index (PII) = 0.42/8	Nov. 1989	Springborn Laboratories, Ohio USA
18	Rabbit NA	NA	Topical	10 on intact skin 3 on abraded skin	Undiluted	2	Intact skin : none to slight exfoliation Abraded skin : slight hyperemia and exfoliation	Dec. 1968	Dow Chemical Company USA
				10 on intact skin 3 on abraded skin	10 % solution in Dowanol DPM	2	Intact skin : none to moderate exfoliation Abraded skin : slight hyperemia and exfoliation	Dec. 1968	Dow Chemical Company USA

NA : Information not available



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MULTIDOSE TOXICITY STUDIES

Ref #	Test/type	Species/ strain	Initial group	Route of administration	Dose	Document ID	Results	Date	Laboratory
19	Subacute (17-22 days) inhalation toxicity study in mice	Mice NA	50 mice (lowest concentration) 20 mice (mid concentration) 45 mice (highest concentration)	Inhalation (whole body) 7 h/day 13 to 15 exposures for 17 to 22 days	35.1, 42 or 58 mg/l	7	Nervous signs and mortality with a dose/response relationship	1951	NIH **USA**
20	Subacute (8 days) inhalation toxicity study in rats	Rats NA	One group of 4 F	Inhalation	4000 ppm, 6 hr daily, exposure for 8 days	10	No clinical nor hematological changes. No abnormalities at necropsy	1970	Imperial Chemical Industries **UK**
21	Subchronic (13 weeks) inhalation toxicity study in rats	Rats Wistar	Total : 80 10 M + 10 F per dose	Inhalation (nose only) 6 h/day, 5 d/week, 13 weeks	0 (control) 400, 2000 and 10,000 ppm	11	10,000 ppm : nervous signs and slightly increased liver weight 400 and 2000 ppm : no changes in clinical signs. Hematology-biochemistry-urinalyses-ophthalmology-necropsy-microscopic examination	Sept. 1994	Hoechst AG, Frankfurt **GERMANY**

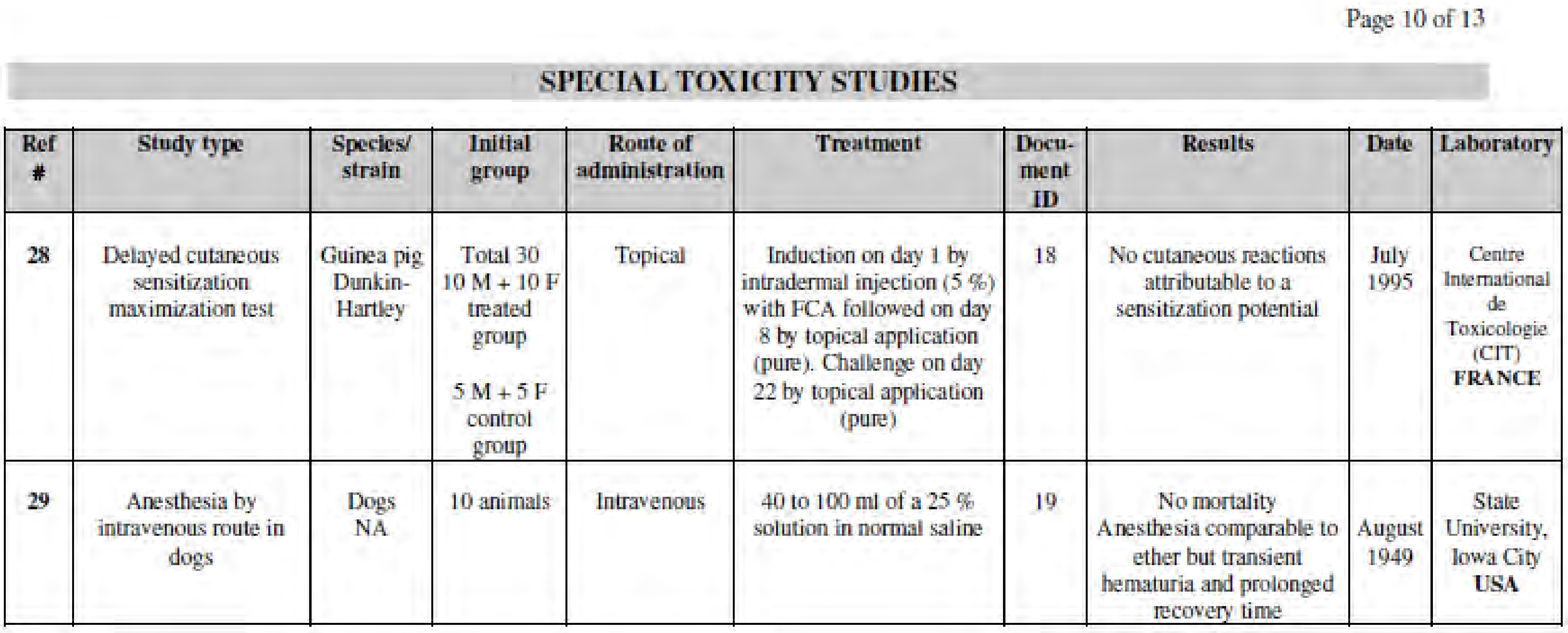
NA : Information not available

REPRODUCTION STUDIES

Ref #	Study type	Species/ Strain	Initial Group	Route of Admini-stration	Dose PPM	Treatment duration	Docu-ment ID	Maternal Toxicity	Embryo/ foetotoxicity	Comments	Date	Laboratory
22	Dose range finding study by inhalation administration in the pregnant rat	Rat Charles River	Total 40 1 control and 3 treated groups 10 mated females each	Inhalation 6 hour daily exposure	0 (control) 400 2000 10,000	From day 6 to 15 of pregnancy	12	At 400 and 2000 ppm no observable effects on the parent female At 10,000 ppm reduction in body weight gain and food intake, increase in water intake	At 400, 2000 and 10,000 ppm no observable effects on the litter para-meters or the macroscopic foetal structure	At 10,000 ppm some clinical signs	1997	Huntingdon Life Science **UK**
23	Effects on embryofoetal development by inhalation in the rat	Rat Charles River	Total 100, 1 control and 3 treated groups of 25 mated females each	Inhalation 6 hour daily exposure	0 (control) 400 2000 10,000	From day 6 to 15 of pregnancy	13	At 386 and 1954 ppm : no treatment-related findings. At 10,068 ppm : reduction in body weight gain between Days 6 and 12 of pregnancy and food intake between Days 6 and 16 of pregnancy. Water intake markedly higher than controls during Days 8 to 19 post coitum.	No changes considered to be related to exposure to methylal. Exposure of the parent female to 10,068 ppm has no effect on embryo-foetal development.	No effect exposure level : 1954 ppm.	1997	Huntingdon Life Science **UK**

MUTAGENICITY STUDIES

Ref #	Study type	Study description	Treatment	Docu-ment ID	Result	Date	Laboratory
24	Ames test	In vitro genotoxicity in S. Typhimurium strains TA 1535, TA 1537, TA 1538, TA 98 and TA 100, with and without metabolic activation in a pre incubation assay with a closed phase incubation	667, 1000, 3333, 6667 and 10,000 µg/plate	14	Mutagenic activity with TA 98 and TA 100 at 10000 µg/plate in absence of metabolic activation No activity at lower concentrations	Sept. 1989	Microbiological associates, MD **USA**
25	Ames test	In vitro genotoxicity in S. Typhimurium strains (TA 1535 - TA 1537 - TA 98 and TA 100) and E. Coli WP 2 uvr A, with and without metabolic activation	Pre-incubation assay : 312.5, 625, 1250, 2500 and 5000 µg/plate Second test : exposure to vapour in air at 5, 10, 20, 40 and 80 % (v/v)	15	No mutagenic activity both in presence or in absence of metabolic activation	July 1996	Huntingdon Life Science **UK**
26	Mutagenicity in the CHO/HGPRT forward mutation assay	Exposure of CHO cells to the test substance and selection of mutants at the HGPRT locus as able to form colonies in the presence of 6-thio-guanine	0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/ml with and without metabolic activation	16	Toxicity at concentrations above 1000 µg/ml No mutagenic activity both in presence or in absence of metabolic activation	Oct. 1990	Hazleton Laboratories, MD **USA**
27	Mouse micronucleus test	Evaluation of the micronuclei in bone marrow polychromatic erythrocytes of mice. 5 M and 5 F ICR mice per dose/harvest time group. Harvest time at 24 h, 48 and 72 h	Single intraperitoneal injection at doses of 400, 1333 and 4000 mg/kg bw	17	No significant increase in micronuclei in bone marrow polychromatic erythrocytes	July 1990	Hazleton Laboratories, MD **USA**



SPECIAL TOXICITY STUDIES

Ref #	Study type	Species/ strain	Initial group	Route of administration	Treatment	Document ID	Results	Date	Laboratory
28	Delayed cutaneous sensitization maximization test	Guinea pig Dunkin-Hartley	Total 30 10 M + 10 F treated group 5 M + 5 F control group	Topical	Induction on day 1 by intradermal injection (5 %) with FCA followed on day 8 by topical application (pure). Challenge on day 22 by topical application (pure)	18	No cutaneous reactions attributable to a sensitization potential	July 1995	Centre International de Toxicologie (CIT) **FRANCE**
29	Anesthesia by intravenous route in dogs	Dogs NA	10 animals	Intravenous	40 to 100 ml of a 25 % solution in normal saline	19	No mortality Anesthesia comparable to ether but transient hematuria and prolonged recovery time	August 1949	State University, Iowa City **USA**

DOCUMENTS

1. ***Methylal : Metabolism and Hygienic Standardization in a Work Environment***

   L.A. Tomilina, Yu. S. Rotenberg, F.D. Mashbits, M.B. Komanovskaia, and L.M. Knizhnikova.

   Gig. Truda, 1984, n° 6, 27-29

2. ***Toxicological Properties and Industrial Handling Hazards of Dimethoxymethane***

   Biochemical Research Laboratory, The Dow Chemical Company

   December 16th, 1968

   EPA/OTS Doc # 86-870002205 (1987)

   NTIS/OTS 0515995

3. ***Methylal : Acute Toxicity and Primary Irritancy Studies in Rats and Rabbits***

   Bushy Run Research Center, Pennsylvania, U.S.A.

   Submitted by the Union Carbide Corporation, Danbury, Connecticut, U.S.A.

   December 7th, 1982

   EPA/OTS Doc # 88-920001329 (1992)

   NTIS/OTS 0536049

4. ***Biochemorphic Aspects of Paraldehyde and Certain Acetals***

   P.K. Knoefel, Lester Lonergan and C.D. Leake.

   Proceedings of the Society for Experimental Biology and Medicine. 29, 730-732 (1932).

5. ***Acute Dermal Toxicity Study in Rabbits with Methylal***

Springborn Laboratories Inc., Spencerville, Ohio, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

November 22nd, 1989

EPA/OTS Doc # 86-900000034 (1989)

NTIS/OTS 0521584

6. ***Single Acute Exposure Dose Selection Study on Methylal***

Hazleton Laboratories America, Inc., Kensington, Maryland, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

June 14th, 1990

EPA/OTS Doc. # 86-900000469 (1990)

NTIS/OTS 0524346

7. ***The Toxicity of Methylal***

F.L. Weaver, Jr., A.R. Hough, B. Highman, L.T. Fairhall

Brit. J. Industr. Med., 1951, 8, 279

8. ***NPIRI Raw Material Data Handbook***
(National Association of Printing Ink Research Institute)

V.I Organic Solvents, 1974, p. 73

9. ***Primary Skin Irritation Study in Rabbits with Methylal***

Springborn Laboratories, Inc., Spencerville, Ohio, U.S.A.

Submitted by Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

November 3rd, 1989

EPA/OTS Doc # 86-900000029 (1989)

NTIS/OTS 0535051

10. ***The Subacute Inhalation Toxicity of 109 Industrial Chemicals***

J.C. Cage

Brit. J. Industr. Med., 1970, 27, 1

11. ***Testing for Subchronic (13 weeks) Inhalation Toxicity in Male and Female Wistar Rats.***

Pharma Development, Corporate Toxicology, Hoechst Aktiengesellschaft, Frankfurt am Main, Germany.

September 27th, 1994

Summary of the 491 page study.

12. ***Methylal. A Dose Range Finding Study by Inhalation Administration in the Pregnant Rat.***

Huntingdon Life Sciences, Ltd., Huntingdon, England.

13. ***Methylal. A Study for Effects on Embryofoetal Development by Inhalation Administration in the Rat.***

Huntingdon Life Sciences, Ltd., Huntingdon, England.

14. ***Salmonella / Mammalian - Microsome Preincubation Mutagenicity Assay with a Closed Phase Incubation System***

Microbiological Associates, Inc., Rockville, Maryland, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

September 20th, 1989.

EPA/OTS Doc # 86-900000004

EPA/OTS 0521278

15. ***Methylal, Bacterial Mutation Assay***

Huntingdon Life Sciences Ltd, Huntingdon, England.

July 23rd, 1996

Study on Salmonella typhimurium (strains TA 1535, TA 1537, TA 98 and TA 100)
Escherichia coli (WP 2 uvr A)

Pre-incubation method

Methylal as a vapour in air

16. ***Mutagenicity Test on Methylal in the CHO/HGPRT Forward Mutation Assay***

Hazleton Laboratories America, Inc., Kensington, Maryland, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

October 10th, 1990

EPA/OTS Doc # 86-910000038 (1990)

NTIS/OTS 0528332

17. ***Mutagenicity Test on Methylal In Vivo Mouse Micronucleus Assay***

Hazleton Laboratories America, Inc., Kensington, Maryland, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

July 25th, 1990

EPA/OTS Doc # 86-900000475 (1990)

NTIS/OTS 0530014

18. ***Skin Sensitization Test in Guinea-Pigs***
(Maximization method of Magnusson, B. and Kligman, A.M.)

Centre international de toxicologie, Evreux, France

July 11th, 1995

19. ***Anesthesia with Methylal in Dogs, Mice and Rats***

Robert W. Virtue.

Anesthesiology, Vol. 12 (1951), 100-108.

ATTACHMENT V
FLAMMABILITY

Flammability properties of an auxiliary blowing agent impact prominently into assessing the conditions of its potential use in the manufacture of PU foams. Before drawing conclusions pertaining to methylal it may be useful to look into the general phenomenon of combustibility.

1. DEFINITIONS

Properties commonly used to define flammable substances are[2]:

- **flash point**: the lowest temperature at which vapors above the liquid will "flash" when exposed to a flame in a standard test apparatus
- **auto-ignition temperature**: the temperature at which a flammable substance will burn spontaneously (without an external ignition source)
- **flammable limits**: concentrations range where a flame will propagate away from an ignition source
- **maximum explosion pressure**: highest buildup of pressure after ignition in a closed vessel
- **maximum rate of pressure rise**: maximum slope of the plot of pressure versus time, after ignition, up to maximum pressure
- **minimum ignition energy**: smallest amount of energy in an electric spark which will ignite a flammable mixture
- **heat of combustion**: the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions

2. APPLICATION TO EXPANSION AGENTS

Combustibility - a blowing agent is commonly stored and processed as a liquid but turns into a gas as part of the foam expansion, due to the exothermic reaction between water and isocyanate (and to a lesser extent polyol and isocyanate), expanding the still liquid reaction mixture and filling the generated foam cells. Addressing the combustibility of a blowing agent as a liquid is equally important as of a gas. For instance, HCFC-141b is not flammable as a liquid but its vapors may still burn. As it easily generates vapors at ambient conditions it should therefore also be tested for gaseous flammable properties. HCFC-141b is therefore frequently listed in an MSDS as “moderately” flammable or simply “yes”[3]. Methylal, on the other side, is even as a liquid flammable (which does not necessarily imply explosive). Its burning profile is very much like alcohol, i.e. it burns with a low energy, blue flame and its energy of combustion is very low—much more like HCFC-141b than like pentanes. Following data show this:

Substance	Heat of Combustion (kcal/g)	Comments
HCFC-141b	1.9	
Methyl Formate	3.9	
Methylal	6.1	
Ethanol	7.1	
Pentane (commercial mix)	11.5	Cyclopentane estimated ~10% lower

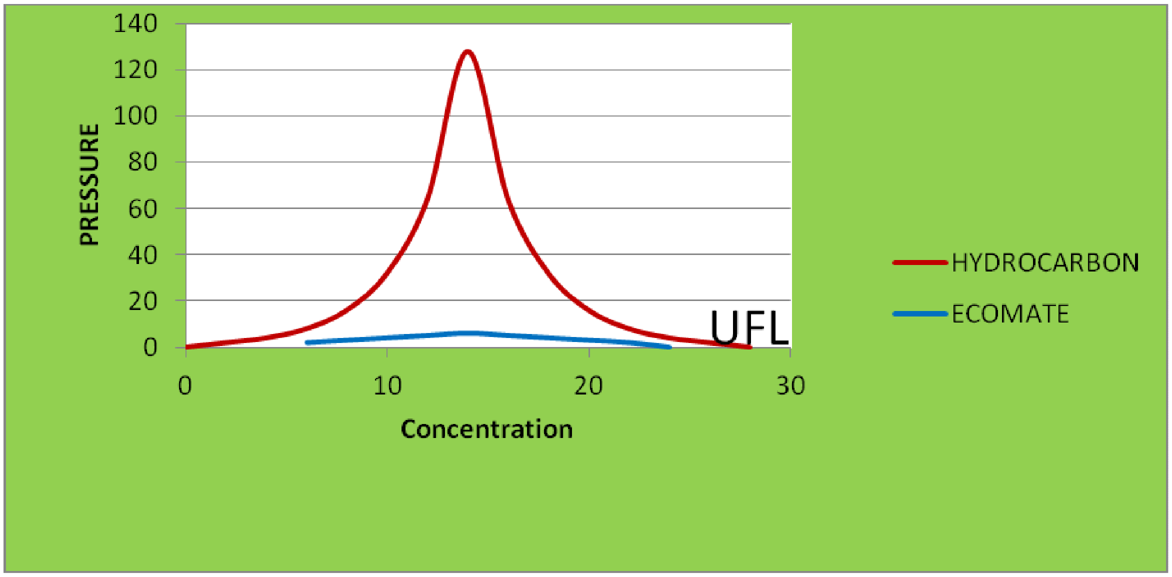
---

[2] Panov, G.E. and Polozkov, V. T.. “Flammable Substances”, Encyclopedia of Occupational Health and Safety, 3rd Edition, International Labor Office Geneva, pp. 881-883 (1983)

[3] Lavelle, J. P., “Flammability Characteristics of HCFC 141b and HCFC-142b”, Journal of Fire Sciences 1989 7; pp 426-439

The relatively low heat of combustion is also the reason that neither HCFC-141b nor ML adds to the fire load of foams the way HCs do. HCFC-containing polyol systems generally are non flammable and the same is the case for ML—**within certain limits.**

Finally, a low heat of combustion decreases the **explosion pressure** and the **maximum rate of pressure rise** as the following picture shows (courtesy FSI; ecomate = methyl formate, the pressure line for methylal would be somewhat higher but still much lower than for hydrocarbons):



Flash Point is commonly used as the primary property to describe the fire hazard of a **liquid**. Pure ML, with its flashpoint of -18^{0}C certainly needs proper safeguarding but that change after blending with products of low combustibility. Tests have shown such systems to be meeting non-flammability labeling criteria by the US-DOT—non-sustained burning at 120^0 F (ASTM D4206-96)—at ML concentrations <2-5% for polyols and <2% for isocyanates. Such concentrations suffice to reformulate low/medium-HCFC-based systems.

Flammable, Flammability, or **Explosive** limits are the primary property describing fire hazards of **gases**. They indicate the proportion of combustible gases in a mixture, between which limits this mixture is flammable and **CAN** be explosive. The lower flammable limit (LFL) describes the leanest mixture that is still flammable, i.e. the mixture with the smallest fraction of combustible gas, while the upper flammable limit (UFL) identifies the richest flammable mixture. A **deflagration** is a propagation of a combustion zone at a speed less than the speed of sound in the un-reacted medium. A **detonation** is a propagation of a combustion zone at a velocity greater than the speed of sound in the un-reacted medium. An **explosion** is the bursting, or rupture, of an enclosure or container due to the development of internal pressure from a deflagration or detonation as defined in NFPA 69. Three essential items for burning a material are fuel, air (oxygen or another oxidizing agent) and an ignition source,

If, under atmospheric conditions, there is not enough fuel, a mixture is considered below the lower flammability limit and it will not burn. Once the fuel-air mixture is within the flammable range, there still must be an ignition source present for it to burn (assuming the temperature is less than the auto-ignition temperature). Given a substance has a flammability range, there are several potential scenarios:

Scenario	**Mitigating Action**
The LFL will not be approached	No action required
The LFL can be approached or exceeded	Exhaust will keep the space under LFL or anti-spark devices such as electrical grounding etc. will eliminate an ignition source
The LFL will be exceeded	Spark arrestors will keep the space free of ignition sources

Mitigation actions for the latter two scenarios are frequently combined and completed with an early warning system (sensors with alarm function).

3. APPLICATION TO METHYLAL

For neither HCFC-141b nor methylal the LFL will be approached under standard process conditions (ambient temperatures 15-40 ^{0}C; substance emissions under legal exposure limits) as the following calculations show:

Methylal

- LFL = 1.6% in air by volume = 220 g/m^3 = 5,700 ppm
- Maximum concentration allowed by OSHA.NIOSH/ACGIH:
  - TWA = 1,000 ppm = 220 mg/m^3 =**17% of LFL**
  - STEL = 1,250 ppm = 275 mg/m^3 = **22% of LFL**

HCFC-141b

- LEL = 7.4% in air by volume = 925 g/m^3 = 193,000 ppm
- Maximum concentration allowed (WEEL):
  - TWA = 500 ppm = 2,4 g/m^3 = **0.26% of LFL**
  - STEL = 3,000 ppm = 14.4 g/m^3 = **1.56% of LFL**

The margin of 4.5-6 of the maximum allowable vapor concentration compared to the LFL is not a very comfortable one. One should, however, also take into account that blends of polyols with methylal show a low tendency to combustion (Lambiotte) as the following data show:

Blend (php)		Combustion Description (in the presence of a flame)
Polyol (viscosity 930 mPa.s)	Methylal	
98	2	No ignition
96	4	No ignition
94	6	No ignition
92	8	No ignition
90	10	Single ignition of the vapors; no further ignition in presence of a flame
88	12	Ignition of the vapors; can be repeated but is self-extinguishing
86	14	Continuous burning; no detonation

4. CONCLUSIONS/RECOMMENDATIONS

- Methylal as a pure liquid is very flammable and requires proper safeguards. The risk of detonation or explosion is, however, remote because its low heat of combustion;
- A PU system based on 1-5 php methylal in the polyol or 2-7.5 php methylal in the polyol and MDI can be formulated as a low combustible liquid and will not reach the LFL;
- PU systems with methylal exceeding that concentration are flammable liquids and need to be labeled as such. However, if applicable TWA and STEL limits are met, the emissions will not be of concern, although the safety margin of 4.5-6 is not a very comfortable one and would require close monitoring of adherence to these thresholds.

In view of the foregoing, following recommendations are offered:

1. System houses, who process pure grade methylal should have

    - Proper personal protective equipment;
    - Closed blending containers, with a dry nitrogen blanket;
    - Explosion proof equipment (pump, agitator, light, heating/cooling,);
    - Electrically grounded equipment and drums (grounding clip);
    - A methylal vapor sensor with alarm function set on 20% LFL;
    - Adequate ventilation;
    - Meter Methylal under the level of the liquid to which it is being added.

2. Downstream users, who process polyol and/or Isocyanate blends should have

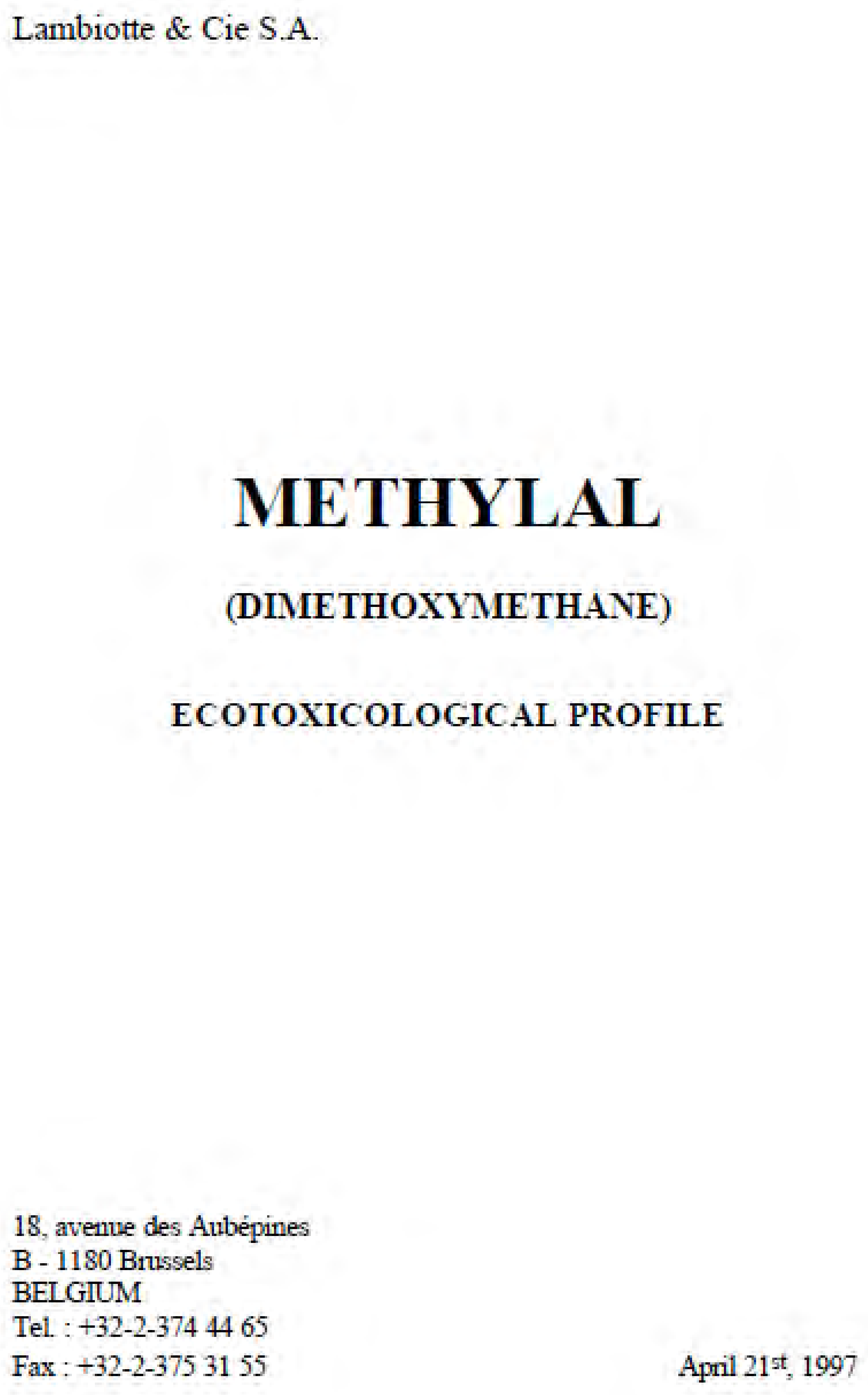
    - Proper personal protective equipment;
    - Electrically grounded equipment and drums (grounding clip);
    - A methylal vapor sensor with alarm function set on 20% LFL;
    - Adequate ventilation.

In all cases, the relevant MSDS and OSHA's Occupational Health Guideline for Methylal or similar applicable in the country of residence should be applied.

5.

ATTACHMENT VI

ECOTOXICOLOGICAL PROFILE



Lambiotte & Cie S.A.

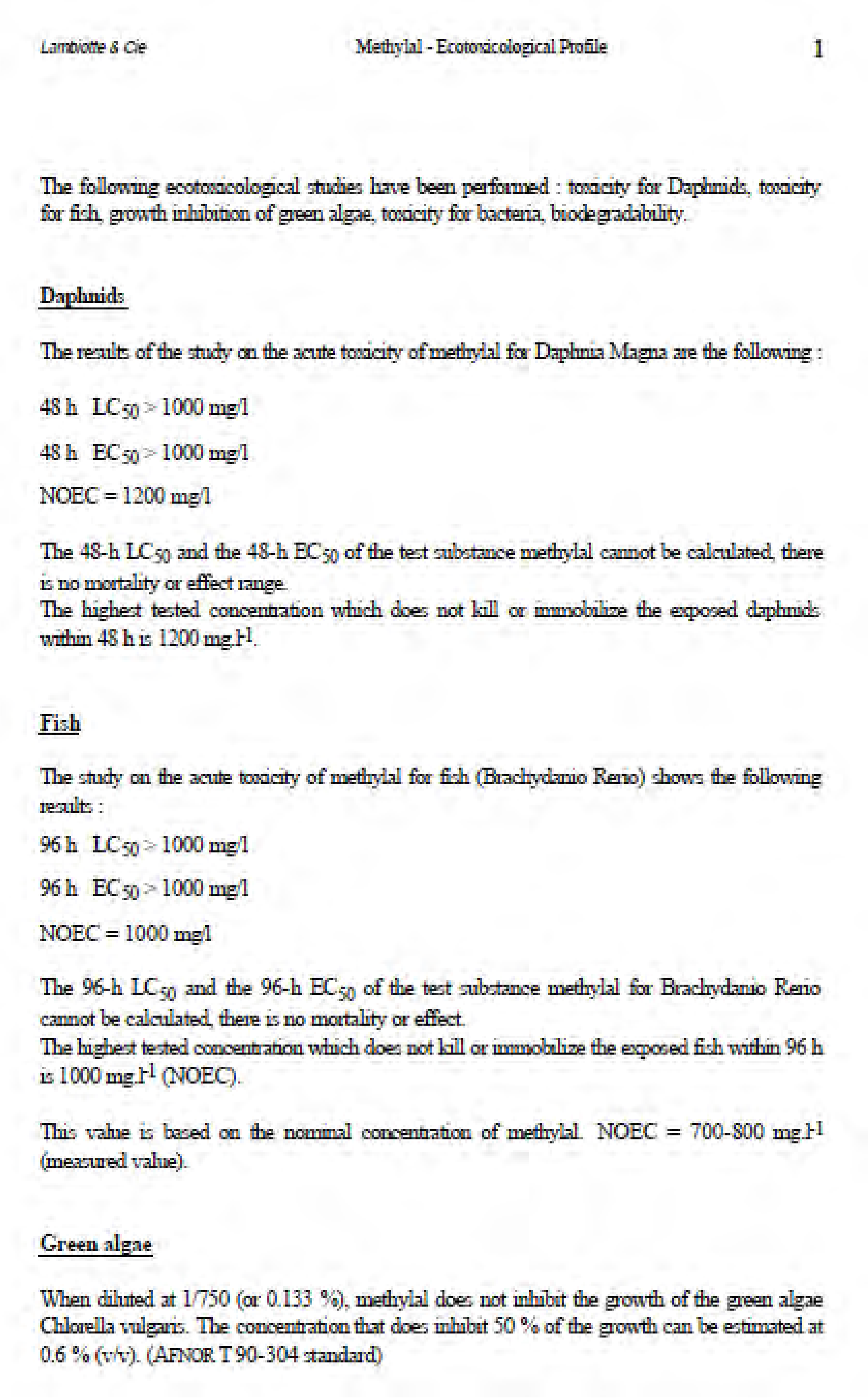
METHYLAL

(DIMETHOXYMETHANE)

ECOTOXICOLOGICAL PROFILE

18, avenue des Aubépines
B - 1180 Brussels
BELGIUM
Tel. : +32-2-374 44 65
Fax : +32-2-375 31 55

April 21st, 1997



The following ecotoxicological studies have been performed : toxicity for Daphnids, toxicity for fish, growth inhibition of green algae, toxicity for bacteria, biodegradability.

Daphnids

The results of the study on the acute toxicity of methylal for Daphnia Magna are the following :

48 h $LC_{50} > 1000$ mg/l

48 h $EC_{50} > 1000$ mg/l

NOEC = 1200 mg/l

The 48-h LC_{50} and the 48-h EC_{50} of the test substance methylal cannot be calculated, there is no mortality or effect range.
The highest tested concentration which does not kill or immobilize the exposed daphnids within 48 h is 1200 $mg.l^{-1}$.

Fish

The study on the acute toxicity of methylal for fish (Brachydanio Rerio) shows the following results :

96 h $LC_{50} > 1000$ mg/l

96 h $EC_{50} > 1000$ mg/l

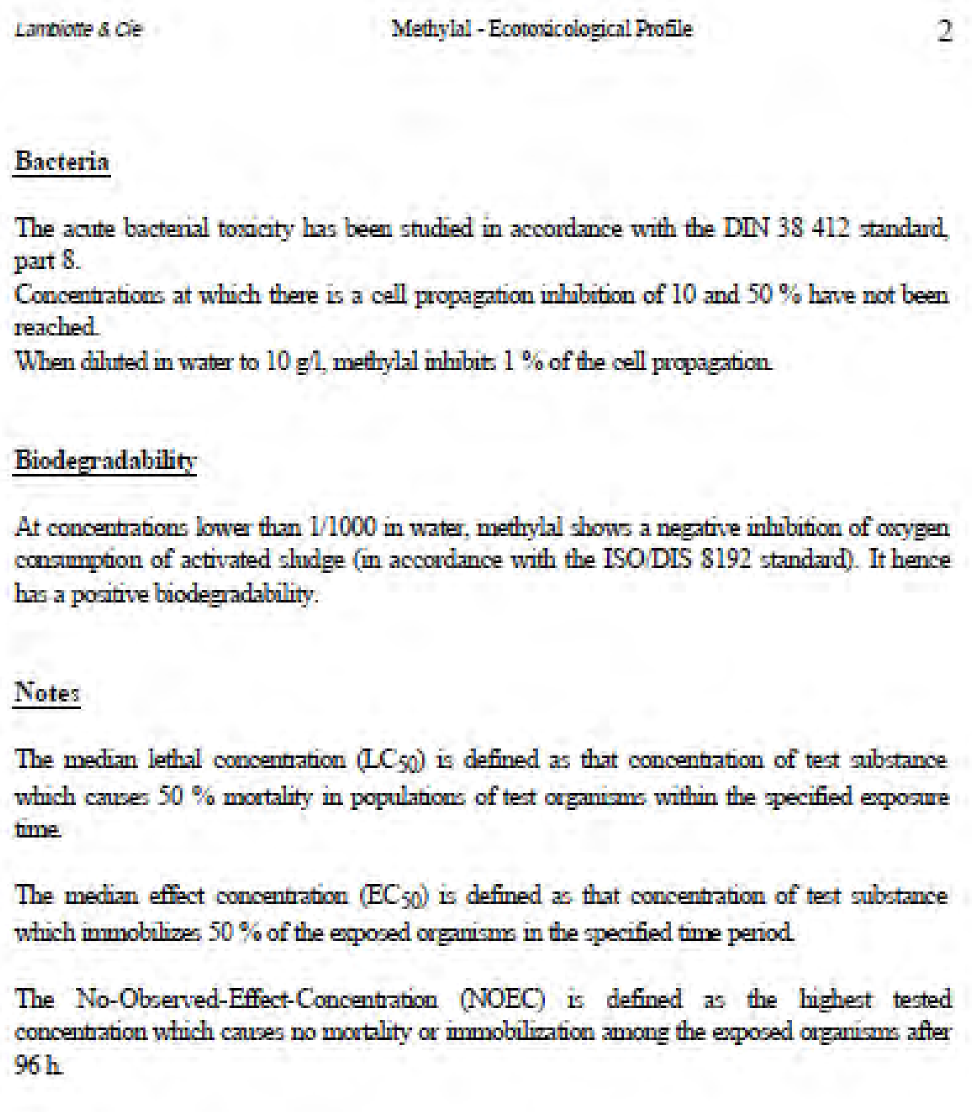
NOEC = 1000 mg/l

The 96-h LC_{50} and the 96-h EC_{50} of the test substance methylal for Brachydanio Rerio cannot be calculated, there is no mortality or effect.
The highest tested concentration which does not kill or immobilize the exposed fish within 96 h is 1000 $mg.l^{-1}$ (NOEC).

This value is based on the nominal concentration of methylal. NOEC = 700-800 $mg.l^{-1}$ (measured value).

Green algae

When diluted at 1/750 (or 0.133 %), methylal does not inhibit the growth of the green algae Chlorella vulgaris. The concentration that does inhibit 50 % of the growth can be estimated at 0.6 % (v/v). (AFNOR T 90-304 standard)



Bacteria

The acute bacterial toxicity has been studied in accordance with the DIN 38 412 standard, part 8.
Concentrations at which there is a cell propagation inhibition of 10 and 50 % have not been reached.
When diluted in water to 10 g/l, methylal inhibits 1 % of the cell propagation.

Biodegradability

At concentrations lower than 1/1000 in water, methylal shows a negative inhibition of oxygen consumption of activated sludge (in accordance with the ISO/DIS 8192 standard). It hence has a positive biodegradability.

Notes

The median lethal concentration (LC_{50}) is defined as that concentration of test substance which causes 50 % mortality in populations of test organisms within the specified exposure time.

The median effect concentration (EC_{50}) is defined as that concentration of test substance which immobilizes 50 % of the exposed organisms in the specified time period.

The No-Observed-Effect-Concentration (NOEC) is defined as the highest tested concentration which causes no mortality or immobilization among the exposed organisms after 96 h.

ATTACHMENT VII
SAMPLE FORMULATIONS

POUR IN PLACE

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	83,16	100,00	82,08	100,00
Cross-linker	0,92	1,11	0,90	1,10
Silicone	0,27	0,32	0,11	0,13
Additive	2,08	2,50	0,00	0,00
Catalyst A	0,83	1,00	0,52	0,63
Catalyst B	1,00	1,20	0,56	0,68
Water	1,24	1,49	1,22	1,48
Methylal	10,50	12,63	0,00	0,00
HCFC-141b	0,00	0,00	14,61	17,80
Total	100,00	120,25	100,00	121,82

STRUCTURAL FOAM

	Methylal		HCFC-141b	
	%	pph	%	pph
Rigid polyol	57,62	70,00	56,00	70,00
Moulded polyol	24,70	30,00	24,00	30,00
Cross-linker	5,14	6,24	5,00	6,25
Glycol	5,14	6,24	5,00	6,25
Silicone	1,54	1,87	1,50	1,87
Catalyst	1,54	1,87	1,50	1,87
Water	0,21	0,25	0,20	0,25
Methylal	4,11	5,00	0,00	0,00
HCFC-141b	0,00	0,00	6,80	8,50
Total	100,00	121,47	100,00	124,99

NON-CONTINUOUS BLOCK

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	60,61	79,00	55,27	85,00
Polyol B	8,44	11,00	6,50	10,00
Polyol C	7,67	10,00	3,25	5,00
Cross-linker	0,00	0,00	2,60	4,00
TCPP	11,51	15,00	8,45	13,00
Silicone	0,81	1,05	1,30	2,00
Catalyst	0,23	0,30	0,00	0,00
Catalyst A	0,00	0,00	0,44	0,67
Catalyst B	0,00	0,00	0,12	0,18
Water	1,53	2,00	1,26	1,93
Methylal	9,20	12,00	0,00	0,00
HCFC-141b	0,00	0,00	20,81	32,00
Total	100,00	130,35	100,00	153,78

SPRAY

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	52,47	70,00	43,03	69,97
Polyol B	22,49	30,00	18,47	30,03
TCPP	12,19	16,27	9,98	16,23
Silicone	1,21	1,62	0,00	0,00
Catalyst A	0,61	0,81	0,50	0,81
Catalyst B	0,07	0,09	0,06	0,10
Water	1,22	1,63	1,00	1,62
Methylal	9,74	13,00	0,00	0,00
HCFC-141b	0,00	0,00	26,96	43,83
Total	100,00	133,42	100,00	162,59

TRANSPORTATION

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	61,60	80,00	55,70	80,00
Polyol B	15,40	20,00	13,92	20,00
Cross-linker	3,31	4,30	2,99	4,30
TCPP	10,01	13,00	9,05	13,00
Silicone	1,15	1,50	1,04	1,50
Amine A	0,08	0,10	0,10	0,14
Amine B	0,69	0,90	0,97	1,40
Water	1,60	2,08	0,91	1,30
Methylal	6,16	8,00	0,00	0,00
HCFC-141b	0,00	0,00	15,32	22,00
Total	100,00	129,88	100,00	143,64

THERMOWARE

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	77,28	100,00	69,33	100,00
TCPP	10,05	13,00	9,01	13,00
Silicone	1,31	1,70	0,55	0,80
Catalyst A	0,46	0,60	0,19	0,27
Catalyst B	0,85	1,10	0,55	0,80
Catalyst C	0,00	0,00	0,76	1,10
Water	2,32	3,00	1,59	2,30
Methylal	7,73	10,00	0,00	0,00
HCFC-141b	0,00	0,00	18,02	26,00
Total	100,00	129,40	100,00	144,27

WATER HEATER

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	0,00	0,00	72,15	100,00
Polyol A	79,00	95,00	0,00	0,00
Polyol B	4,15	5,00	0,00	0,00
Cross-linker	0,00	0,00	2,89	4,00
TCPP	6,64	8,00	9,38	13,00
Silicone	1,50	1,90	0,87	1,20
Catalyst	0,66	0,80	0,00	0,00
Catalyst A	0,00	0,00	0,43	0,60
Catalyst B	0,00	0,00	0,29	0,40
Water	1,41	1,70	1,01	1,40
Methylal	6,64	8,00	0,00	0,00
HCFC-141b	0,00	0,00	12,98	18,00
Total	100,00	120,40	100,00	138,60

HIGH RESILIENCE MOLDED

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	73,09	79,22	73,09	80,00
Copolymer	19,18	20,78	18,27	20,00
Silicone	0,46	0,50	0,46	0,50
Catalyst A	0,73	0,79	0,73	0,80
Catalyst B	0,34	0,37	0,34	0,35
Water	3,46	3,75	3,46	3,79
Methylal	2,74	2,97	0,00	0,00
HCFC-141b	0,00	0,00	3,65	4,00
Total	100,00	108,38	100,00	109,44

VISCOELASTIC

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	75,00	80,50	74,30	80,50
Polyol B	16,15	17,30	16,00	17,33
Polyol C	2,02	2,20	2,00	2,17
Silicone A	0,25	0,27	0,25	0,27
Silicone B	1,01	1,08	1,00	1,08
Catalyst A	0,15	0,16	0,15	0,16
Catalyst B	0,30	0,32	0,30	0,32
Water	3,00	3,22	3,00	3,25
Methylal	2,12	2,27	0,00	0,00
HCFC-141b	0,00	0,00	3,00	3,25
Total	100,00	107,32	100,00	108,33

VISCOELASTIC BLOCKS (NON CONTINOUS)

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	22,88	24,23	22,88	24,38
Polyol B	22,87	24,22	22,87	24,37
Polyol C	17,44	18,47	17,44	18,58
Polyol D	19,16	20,29	19,16	20,41
Polyol E	3,83	4,06	3,83	4,08
Polyol F	8,24	8,73	7,68	8,18
Silicone A	0,48	0,51	0,48	0,51
Silicone B	0,58	0,61	0,58	0,62
Catalyst A	0,09	0,09	0,09	0,09
Catalyst B	0,38	0,40	0,38	0,40
Water	2,25	2,38	2,25	2,39
Methylal	1,80	1,91	0,00	0,00
HCFC-141b	0,00	0,00	2,36	2,51
Total	100,00	105,90	100,00	106,52

STEERING WHEELS

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	79,48	100,00	78,48	100,00
Cross-linker	6,70	8,54	6,70	8,54
Silicone	0,22	0,28	0,22	0,28
Colorant	3,00	3,82	3,00	3,82
Amine	0,60	0,76	0,60	0,76
Methylal	10,00	12,74	0,00	0,00
HCFC-141b	0,00	0,00	11,00	14,02
Total	100,00	126,14	100,00	127,42

FURNITURE

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	87,11	100,00	83,88	100,00
Cross-linker	7,26	8,34	7,25	8,64
Silicone	0,24	0,28	0,24	0,29
Amine	0,64	0,73	0,63	0,75
Methylal	4,75	5,41	0,00	0,00
HCFC-141b	0,00	0,00	8,00	9,54
Total	100,00	114,80	100,00	119,22

ATTACHMENT VIII

PARTICIPATION LETTERSOF DOWNSTREAM USERS

MATERIAL SAFETY DATA SHEET

METHYLAL TECHNICAL GRADE

Page : 1
Revision nr : 5
Date : 30/9/2005
Supersedes : 20/2/2004

L-9307
www.lisam.com

Highly flammable
Harmful

Producer
Lambiotte & Cie s.a.
Grand' Rue, 79
B-6724 Marbehan Belgique-Belgie
Tel. +32 (0)63 41 00 80
EMERGENCY : +32 (0)70 245 245

1. Identification of the product and the company

Company identification : See distributor.
Trade name : METHYLAL TECHNICAL GRADE.
Chemical family : Acetal.
Type of product : Liquid.
Use : Industrial.

2. Information on ingredients

This product is considered to be hazardous and contains hazardous components.

Substance name		Value(s)	CAS nr / EINECS nr / EC index	Symbol(s)	R-Phrase(s)
Methylal	:	> 93 %	000109-87-5 / 203-714-2 / -----	F	11
Methanol	:	<= 6.5 %	000067-56-1 / 200-659-6 / 603-001-00-X	F T	11-23/24/25-39/ 23/24/25

3. Hazards identification

Risk Phrases : Harmful by inhalation, in contact with skin and if swallowed.
Dangerous substances : Highly flammable.
Primary route of exposure : Vapours inhalation. Skin contact.
Symptoms relating to use
- Inhalation : Symptoms of overexposure to vapours include : Headache. Dizziness. Drowsiness. Nausea.
- Skin contact : Absorbed through the skin. Redness.
- Eye contact : Direct contact with the eyes is likely irritating.
- Ingestion : Abdominal pain, nausea. Swallowing a small quantity of this material presents some health hazard. Must not come into contact with food or be consumed.

4. First aid measures

First aid
- Inhalation : If overcome by exposure, remove victim to fresh air immediately. Obtain medical attention if breathing difficulty persists.
- Skin contact : Remove affected clothing and wash all exposed skin area with mild soap and water, followed by warm water rinse.
- Eye contact : Rinse immediately with plenty of water. Obtain medical attention if pain, blinking or redness persist.
- Ingestion : If swallowed, immediately administer water (1/2 liter) only if victim is completely conscious/alert and induce immediately vomiting. Seek medical attention immediately.

5. Fire - fighting measures

Flammable class : This product is flammable.
Prevention : No smoking. Keep away from sources of ignition.
Extinguishing media : Foam. Dry chemical. Carbon dioxide. Large quantity of water.
Surrounding fires : Use water spray or fog for cooling exposed containers.
Special exposure hazards : Vapor mixes readily with air, forming explosive mixtures.
Protection against fire : All fire-fighting personnel must wear safety suits. Use self-contained breathing apparatus when in close proximity to fire.
Special procedures : Exercise caution when fighting any chemical fire.

6. Accidental release measures

Personal precautions : Equip cleanup crew with proper protection.
Environmental precautions : Prevent entry to sewers and public waters. Notify authorities if liquid enters sewers or public waters.
After spillage and/or leakage : Clean up any spills as soon as possible, using an absorbent material to collect it. Use suitable disposal containers.

7. Handling and storage

General : No naked lights. No smoking.
Precautions in handling and storage : Do not use compressed air to either agitate or transfer the contents of storage containers (tanks) / shipping drums containing this material.
Technical protective measures : Ground well. Use only non-sparking tools. Use special care to avoid static electric charges.
Storage : Keep container closed when not in use. Store in dry, cool, well-ventilated area.
Storage - away from : Heat sources.
Handling : Handle in accordance with good industrial hygiene and safety procedures. Wash hands and other exposed areas with mild soap and water before eat, drink or smoke and when leaving work.

8. Exposure controls / personal protection

Personal protection
- Respiratory protection : Approved dust or mist respirator should be used if airborne particles are generated when handling this material.
- Skin protection : Wear suitable gloves resistant to chemical penetration.
- Eye protection : Even though no specific eye irritation data is available, wear eye protection appropriate to conditions of use when handling this material.
- Ingestion : When using, do not eat, drink or smoke.

Industrial hygiene : Provide local exhaust or general room ventilation to minimize dust and/or vapour concentrations.

9. Physical and chemical properties

Physical state : Volatile liquid.
Colour : Colourless.
Odour : Ethereal.
pH value : No data available.
Molecular weight : 76.08
Melting point [°C] : -104.8
Initial boiling point [°C] : 42.3
Density : .861
Viscosity : cP (30°C) .325

9. Physical and chemical properties (continued)

Solubility in water [% weight] : 32.3
Flash point [°C] : -18
Auto-ignition temperature [°C] : 237
Explosion limits - lower [%] : 1.6
Explosion limits - upper [%] : 38.5

10. Stability and reactivity

Hazardous decomposition products : Thermal decomposition generates : Carbon dioxide.
Hazardous reactions : Reacts with : Strong acids.
Hazardous properties : Vapor mixes readily with air, forming explosive mixtures.
Conditions to avoid : Heat. Sparks. Open flame.

11. Toxicological information

Rat oral LD50 [mg/kg] : 5620
Rabbit dermal LD50 [mg/kg] : No data available.
Rat inhalation LC50 [mg/kg] : No data available.

12. Ecological information

48 H-CE50 - Daphnia magna [mg/l] : No data available.
Persistence and degradability : Biodegradable

13. Disposal considerations

Disposal : Dispose in a safe manner in accordance with local/national regulations. Dispose of this material and its container at hazardous or special waste collection point.

14. Transport information

Hazard Label(s)

: Flammable. Harmful.
- Proper shipping name : UN 1234 METHYLAL, 3, II
- UN No. : 1234
- H.I. nr : : 33
- ADR/RID : Group : II
  Class : 3
- IMO-IMDG code : Class 3

- EMS-Nr : F-E S-D

UN Packing group : II

15. Regulatory information

Symbol(s) : Harmful.
R Phrase(s) : R11 - Highly flammable.
R20/21/22 - Harmful by inhalation, in contact with skin and if swallowed.
R68/20/21/22 - Harmful : possible risk of irreversible effects through inhalation, in contact with skin and if swallowed.
S Phrase(s) : S03 - Keep in a cool place.

15. Regulatory information (continued)

S09 - Keep container in a well-ventilated place.
S16 - Keep away from sources of ignition - No smoking.
S24 - Avoid contact with skin.
S33 - Take precautionary measures against static discharges.
S35 - This material and its container must be disposed of in a safe way.
S36/37 - Wear suitable protective clothing and gloves.
S53 - Avoid exposure - obtain special instructions before use.
S59 - Refer to manufacturer/supplier for information on recovery/recycling.

16. Other information

Further information : None.

The contents and format of this MSDS are in accordance with EEC Commission Directive 2001/58/EEC.

DISCLAIMER OF LIABILITY The information in this MSDS was obtained from sources which we believe are reliable. However, the information is provided without any warranty, express or implied, regarding its correctness. The conditions or methods of handling, storage, use or disposal of the product are beyond our control and may be beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal or the product. This MSDS was prepared and is to be used only for this product. If the product is used as a component in another product, this MSDS information may not be applicable.

End of document

Occupational Health Guideline for Methylal

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3OCH_2OCH_3$
- Synonyms: Dimethoxymethane; methyl formal; formal; dimethylacetal formaldehyde
- Appearance and odor: Colorless liquid with a pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylal is 1000 parts of methylal per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3100 milligrams of methylal per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylal can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methylal may cause irritation of the eyes, nose, and throat, lightheadedness, incoordination, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure to methylal may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylal.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylal at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylal exposure.

—Skin disease: Methylal is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methylal is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methylal is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylal might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylal vapor is a mild respiratory irritant with anesthetic properties. Mice exposed at 11,000 ppm showed mild irritation of the eyes and respiratory tract, as well as incoordination; recovery was rapid after single exposures. At 14,000 ppm, mice showed more respiratory irritation, occasional pulmonary edema, and a greater degree of anesthesia. At the LC50 level of approximately 18,000 ppm, animals died of bronchopneumonia with fatty changes in the liver, kidney, and heart. At 4000 ppm rats were unaffected by daily 6-hour exposures.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Skin irritation may be expected due to defatting action by the solvent, and eye irritation if splashing occurs. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76
2. Boiling point (760 mm Hg): 44 C (111 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of methylal): 2.6
5. Melting point: −105 C (−157 F)
6. Vapor pressure at 20 C (68 F): 330 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 33
8. Evaporation rate (butyl acetate = 1): 23.1

- **Reactivity**

1. Conditions contributing to instability: Heat, presence of acids
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde, and methyl alcohol) may be released in a fire involving methylal.
4. Special precautions: Methylal will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −18 C (−4 F) (closed cup)
2. Autoignition temperature: 237 C (459 F)
3. Flammable limits in air, % by volume: Lower: 1.6; Upper: 17.6
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold, but Browning notes that it has a slightly pungent odor.
2. Eye Irritation Level: Grant states that "exposures of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially were found to cause . . . occasional irritation of the eyes but no histologically demonstrable abnormality of the optic nerve or retina."

Patty reports that mice which had received 15 7-hour exposures at 11,000 ppm experienced only mild irritation.

No quantitative information is available, however, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Since there is no useful quantitative information relating warning properties to air concentrations of methylal, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methylal vapors using an adsorption tube with subsequent desorption with hexane and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylal may be used. An analytical method for methylal is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylal.
- Clothing wet with liquid methylal should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylal from the clothing. If the clothing is to be laundered or

otherwise cleaned to remove the methylal, the person performing the operation should be informed of methylal's hazardous properties.

- Any clothing which becomes wet with liquid methylal should be removed immediately and not reworn until the methylal is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylal may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methylal should be promptly washed or showered to remove any methylal.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylal may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent for adhesives, resins, gums, waxes, and protective coatings; use as a solvent for extraction of alkaloids, barbituates, organic acids, and hydroxy-acids	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of artificial resins; use as a gasoline and diesel fuel additive; use as a special fuel for rocket and jet engines	General dilution ventilation; process enclosure; personal protective equipment
Use as a reaction solvent with acetylene or in Grignard and Reppe reaction; use as a source of formaldehyde and methanol	General dilution ventilation; process enclosure; personal protective equipment
Use as a methylating agent or chemical intermediate	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of perfume	General dilution ventilation; process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methylal gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methylal gets on the skin, promptly wash the contaminated skin with water, if the methylal has not already evaporated. If methylal soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methylal, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methylal has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methylal is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Methylal should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Methylal may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methylal," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.
- Celanese Corporation: *Product Bulletin – Methylal*, New York.
- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Weaver, F. L., et al.: "Toxicity of Methylal," *British Journal of Industrial Medicine*, 8:279-283, 1951.

RESPIRATORY PROTECTION FOR METHYLAL

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

AIHA LAP, LLC
ACCREDITED LABORATORY
INDUSTRIAL HYGIENE
ISO/IEC 17025:2005
WWW.AIHAACCREDITEDLABS.ORG
LAB # 102800

Relatório de Análise nº 107006.10.11

Cliente Contratante/Avaliado: ARINOS QUÍMICA LTDA.
Rua Arinos, 15 - Parque Industrial Água Vermelha - Osasco - SP - CEP 06276-032
CNPJ 01.722.256/0001-75
Sr. Mario Cezar da Silva

Amostra: Ar ambiental
Recebida em: 14/10/2011
Data da análise: 20/10/2011

Método: NIOSH 1611.

Amostra	Nº do Cliente	Vol./Tempo	Coleta	Resultados	
107006.1	000090109	2,28 L	13/10/2011	Metilal 6,5 ppm	---
107006.2	000077662	3,00 L	13/10/2011	Metilal <2,6 ppm	---

Notas

1 - Amostragem: realizada pela Environ Científica. O relatório de amostragem encontra-se anexado. O resultado e dados são válidos somente para a amostra analisada.
2 - BC: não apresentou massa acima do limite de quantificação.
3 - O resultado foi corrigido pelo branco de meio que não apresentou massa acima do limite de quantificação.
4 - A fase secundária das amostras não apresentou o analito acima de 10 % em relação à fase frontal. Concentrações superiores a 10 % na fase secundária indicam a possibilidade de perda.
5 - As amostras foram recebidas acondicionadas conforme previsto na metodologia.
6 - O resultado precedido de "<" significa que não foi detectado o analito acima do limite de quantificação.

Limites de Quantificação:

Metilal 20 µg.

Siglas:

BC = branco de campo; LQ = limite de quantificação; ppm = parte por milhão; ppb = parte por bilhão; mg/m³ = miligrama por metro cúbico; mg = miligrama; µg = micrograma; NI = não informado; "<" = abaixo do LQ; f/cc = Fibra por centímetro cúbico; NE = não estabelecido.

São Bernardo do Campo, 31/10/2011

Oscar Shigueo Umemura
CRQ IV 04218265
Supervisor do Laboratório

Não é permitida a reprodução parcial deste documento sem a autorização por escrito.

Suzano 19 de agosto de 2011

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma **VISCOELÁSTICA E HIPER SOFT.**

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: Helton Luiz de Araújo Santos

Cargo: Espumador

Empresa: Techfoam Ind.Comercio Ltda
TECHFOAM IND. E COM. LTDA

BLITZ
PROJETOS ESPECIAIS
Sempre uma idéia melhor!

Ribeirão Pires, 29 de julho de 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma Integral skin, Rigido Estrutural e Semirrígido.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: Klaus Dieter Schnur
Cargo: Diretor Comercial
Empresa: Blitz Indústria e Comércio de Plásticos Ltd.

SOPRANO
Um universo de possibilidades.

Farroupilha - RS, 03 de março, 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma rígida.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: ROBSOM COLOMBO BALBIMOT
Cargo: Analista de Processo
Empresa: Soprano

Local, data, ano

CAMBÉ PR 01/06/2011

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do Sistema de Poliuretano, ***Aripol 514FR*** da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação, para produção de espuma rígida por injeção.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

09.402.716/0001-90
90432582-11
EQUIPAMENTOS RODOVIÁRIOS ROMA LTDA.
Rod. Celso Garcia Cid, 2451 - PR 445
Jd. Rian - CEP 86187-000
CAMBÉ — PR

Nome: CLODOALDO BALSANELO

Cargo: ENCARREGADO PRODUÇÃO

Empresa: FURGÃO ROMA

POLITECH®
POLIURETANOS

Porto Alegre, Maio de 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma de Bloco Rígido.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: Sérgio José Correa

Cargo: Diretor Comercial

PURAPELE

MANUFATURA DE PELES FLORENSE LTDA.

VILA NOVA ROMA - 95270-000 - FLORES DA CUNHA - RS
FONE / FAX: (054) 292-2130
INSC. CGCMF Nº 89.968.390/0001-00 - INSC. ESTADUAL Nº 048/0002630

Flores da Cunha - RS, 03 de março, 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma Flexível Moldado.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como, aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: CIRIO SIGNORI

Cargo: DIRETOR

Empresa: Manufatura de Peles Florense Ltda.

Cook Machine

MF COZINHAS INDUSTRIAIS LTDA
R: Herculano de Freitas, 99 - Fundação São Caetano do Sul S.P.
CEP 09520-280 – Fone/Fax: 0xx 11 4223-5060
E-MAIL: cookmachine@mfcozinhas.com.br
Home Page: www.mfcozinhas.com.br

São Caetano do Sul, 14 de Abril de 2011

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da ARINOS QUÍMICA LTDA contendo o agente de expansão METHYLAL incorporado na formulação para produção de espuma Rígida de Isolamento Térmico usada para fabricação de balcões refrigerados.

O resultado obtido na aplicação com o sistema incorporado com METHYLAL apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com METHYLAL atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente

MF COZINHAS INDUSTRIAIS LTDA.

Silvia Maria Ap. Saltini Filleti
Diretora

isar
Isolamentos
Térmicos e Acústicos

Qualidade Certificada · isar
ISO 9001:2000

São Paulo, 07 de Abril de 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma Rígida de Isolamento Térmico em aplicação por Spray.
O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.
Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Rafael Siais Furtado
Diretor Comercial
Isar Isolamentos Térmicos e Acústicos Ltda

Poliuretanos
Brasil

Santana de Parnaíba, 07 de abril de 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma semi-rígida com aplicação em embalagens.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

POLIURETANOS BRASIL LTDA
Rafael Santamaria Sarmento

vittaflex
espumas especiais

Declaração

Declaramos para os devidos fins que realizamos teste de sistema da ***Arinos Química LTDA*** Contendo o agente de expansão ***Methylal*** incorporado na formulação para produção de espuma visco elástica.
O resultado obtido na aplicação com o sistema incorporado com ***methylal*** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.
Portanto, o sistema com ***methylal*** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente

Célio Machado

Célio Machado
Químico industrial
Vittaflex

Suzano 19 de agosto de 2011

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma **VISCOELÁSTICA E HIPER SOFT.**

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: Helton Luiz de Araújo Santos

Cargo: Espumador

Empresa: Techfoam Ind.Comercio Ltda

TECHFOAM IND. E COM. LTDA

LOW COST OPTIONS FOR THE USE OF HYDROCARBONS IN THE MANUFACTURE OF POLYURETHANE FOAMS

AN ASSESSMENT FOR APPLICATION IN MLF PROJECTS

MARCH 2012

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II. HCFC PHASEOUT TECHNOLOGIES IN PU FOAM APPLICATIONS
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VI. FINAL UPDATE ON ABOVE REPORT

EXECUTIVE SUMMARY

This project is part of a series of assessments conducted by UNDP covering substantially all current commercially available products that have potential or have been proven as blowing agent in foams but have not yet been properly assessed in an A5 context or that could be improved upon. This particular pilot project—the assessment of low cost options when using hydrocarbons as blowing agent—has been executed in Egypt with assistance of an equipment manufacturer and a systems manufacturer.

Hydrocarbon technology is available world-wide, but its implementation requires considerable capital outlays—predominantly related to addressing safety issues. On the other side, operating costs are generally somewhat lower than HCFCs. The objective of this pilot project has been to assess options to lower these capital costs without compromising safety or operating costs. **None of these options, however, should impair safety as currently required.**

This project is different from other pilot projects in that it focuses on optimizing costs and performance of an existing and broadly applied—but expensive—technology. The costs effectively limit the technology to large companies only and have led indirectly to wide-spread use of HCFC-141b in smaller and/or less sophisticated enterprises. While recently, the financial threshold for such projects has increased based on its low-GWP impact, so have equipment costs. Therefore, SMEs can only fall back on environmentally undesirable HFCs, marginally performing water-based systems or hope that the assessment of new technologies—will provide more satisfactory options.

The use of hydrocarbon technology has not materially changed over the last 20 years. It requires costly pre-blending and metering equipment, an explosion-free production area and special safety procedures. Also, in many countries the make-up of the chemical systems have not changed over the years while improvements in additives, polyols, the option of co-blending and more optimizations would allow better results at the same or lower costs.

UNDP saw options for cost reduction in the following areas:

- Preblending at supplier level to delete the need for a preblender plus auxiliaries;
- Direct injection of hydrocarbons which also removes the need for a preblender;
- Introduction of more modern HC blends which would allow for lower densities;

The project was executed in three steps:

1. **Equipment Development –** selected through standard procurement procedures by a qualified equipment supplier
2. **System Development –** selected through standard procurement procedures by a qualified system house including trials at a local foam manufacturer or system house that is willing to conduct these and has the capabilities
3. **Reporting –** This includes an information dissemination inter-regional workshop, followed by a final report to the ExCom on the overall outcome

As equipment UNDP selected a three-module high-pressure dispenser capable to process fully formulated systems as well as direct injection of flammable as well as non-flammable blowing agents.

The equipment meets ATEX 94/9/EC and is in conformity to II 2 Gc IIB T4 as well as the requirements as listed in UNEP/Ozl.Pro/ ExCom/25/54, 1998.

The equipment functioned in the subsequent trials well for HCFC systems (baseline), preblended systems and direct injection. In particular, the dispenser offered

- Excellent repeatability
- Acceptable 3 stream blending
- High efficiency in blowing agent containment, leading to lower densities

For the systems development six different systems were selected:

Application Blowing Agent	Commercial Refrigeration	Discontinuous Panels	Water Heaters
HCFC-141b	System A	System C	System E
Cyclopentane (CP)	System B	System D	System F
Normal Pentane (NP)	System B	System D	

The HCFC-141b systems served to provide a baseline while the choice of pentane isomers reflects current market preferences. All pentane blown systems were evaluated as fully formulated systems (blowing agent included) and as partially blended systems (blowing agent added as a third stream).

All systems were tested on

- Physical and chemical stability of the blends
- System properties of the foams
  (processability, mechanical properties, dimensional stability and thermal properties)

The tests showed that

- Physical and chemical stability of cyclopentane systems under standard conditions for up to six months is confirmed;
- Normal pentane systems are not stable beyond one month;
- For preblended systems, as no preblender along with its auxiliary equipment (tanks, piping, etc) is needed, cost savings of around US$ 100,000 can be expected;
- For direct injection, no direct equipment savings can be expected but, with a much more compact design, savings in layout and storage can still be expected;
- If the lower free density can be "translated" into lower applied density, incremental operational costs savings between of 6% and 8% can be expected compared to HCFC-141b systems. On the other side, transportation costs may increase;
- With direct injection, this could even increase up to 10%;
- K values are 5-8% higher than for HCFC-141b foams but equal to conventional CP foams.
- A slightly higher k-factor and lower reactivity show that the mixer head impingement has suffered from the introduction of a third stream. While improvement could be made with an optimized catalyst package, redesign of the mixing head has been selected as the preferable option;

While all technical statements are considered universally valid, cost statements are to be seen in the Egyptian context only and would need to be adjusted for other regions.

While UNDP has identified several areas where follow-up is needed, it feels that the current results are significant enough to justify immediate publication. Follow-up items are listed out below:

- Tailored safety concepts for each of the two approaches (direct injection, preblended systems);
- Investigation if the observed fact that preblended and directly injected approaches lead to lower free rise densities can be translated into lower (acceptable) product densities as well;
- Mixing head optimization;
- Extending the Direct Injection approach to a cost-effective retrofit model, and
- A costing concept based on this report as well as the follow-up outcome

The outcome of these follow-up investigations will be published in a supplemental report, expected to be presented to the 67th ExCom meeting.

1. Introduction

HCFCs are currently still in use in developing ("A5") countries as blowing agents in polyurethane (PU) foams. To replace these HCFCs, following criteria would ideally apply:

- Chemically /physically stable,
- Soluble in the formulation,
- A suitable boiling point with 25^0C being the target,
- Low thermal conductivity in the vapor phase,
- Non flammable,
- Low toxicity,
- Zero ODP,
- Low GWP,
- Low diffusion rate,
- Based on validated technology,
- Commercially available,
- Acceptable in processing, and
- Economically viable.

CFC phaseout in rigid and integral skin foams has been mostly achieved by replacement through

- Hydrochlorofluorocarbons (HCFCs)
- Hydrocarbons (HCs)
- Carbon dioxide (CO_2), generated from water/isocyanate or applied directly as liquid or gas

In developed (non-A5) countries HCFCs have in the mean time been replaced, for which the following options have been available or are currently under development (see **Attachment-II** for more in depth review):

SUBSTANCE	GWP[1]	MOLECULAR WEIGHT	INCREMENTAL GWP[2]	COMMENTS
HCFC-141b	725	117	Baseline	
CO_2	1	44	-725	Used direct/indirect (from water)
Cyclopentane	11[2]	72	-718	Extremely flammable
HFC-245fa	***1,030***	***134***	***443***	
HFC-365mfc	***794***	***148***	***279***	
HFC-134a	***1,430***	***102***	***522***	
Methyl formate	negligible	60	-725	
Methylal	negligible	76	-725	
Acetone	negligible	58	-725	Used in flexible slabstock
FEA-1100	5	164[4]	-718	Under development
HFO-1234ze	6	114	-719	Recently introduced
HBA-2	<15	<134	>-708	Under development
AFA-L1	<15	<134	>-708	Under development

Green = beneficial GWP effect; red = unfavorable GWP effect

[1] Unless otherwise indicated, taken from IPCC's Fourth Assessment (2007)

[2] Derived from comparing GWPs compared to the baseline on an equimolar base. It should be noted that in practice formulators may make changes such as increased water or ABA blends that impact the GWP effect

[3] From UNEP Foams Technical Options Committee's 2006 report

[4] Calculated from published formulations

With water not satisfactory performing in thermal insulation applications, HFCs high in GWP, hydrocarbons high in investment costs, and HFOs not yet completely developed and/or not yet commercially available in developing countries, there is a need to assess other potential alternatives and, therefore, to investigate newly emerged technologies on their technical, cost, availability and environmental performance.

Decision 55/43 of the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol ("MLF") reflects this by promoting pilot projects aimed at validating technologies in a developing country ("A5") context.

UNDP has prepared a series of pilot projects which, it believes, cover substantially all current commercially available products that have potential or have been proven as blowing agent in foams but have not yet been assessed in an A5 context or that could be improved upon. From the mentioned pilot projects, the assessment of the use of methyl formate (MF) and methylal in non-continuous PU applications have been technically completed while the assessment of cost-effective HC technologies has been substantially completed and the use of HFO-1234ze in extruded polystyrene plank is in the final stage with all experimental work done.

This particular pilot project—the assessment of low cost options when using hydrocarbons as blowing agent—has been executed along with SAIP, an Italian manufacturer of PU foam equipment and Dow Chemical, through its System Development Center in Italy and its system house in Egypt.

Hydrocarbon technology is available world-wide, but its implementation requires considerable capital outlays—predominantly related to addressing safety issues. On the other side, operating costs are generally somewhat lower than HCFCs. The objective of this pilot project is to assess options to lower these capital costs without compromising safety or operating costs. This assessment addresses in sequence

- Design and Execution
- Health, Safety, Environment
- Processability
- Physical properties
- Conversion costs
- Conclusions

UNDP acknowledges with appreciation the cooperation extended by its project partners: SAIP (Italy) and Dow Chemical (Italy and Egypt).

While UNDP has identified several areas where follow-up is needed, it feels that the current results are significant enough to justify immediate publication. Follow-up items are listed out below:

- Tailored safety concepts for each of the two approaches (direct injection, preblended systems);
- Investigation if the observed fact that preblended and directly injected approaches lead to lower free rise densities can be translated into lower (acceptable) product densities as well;
- Mixing head optimization;
- Extending the Direct Injection approach to a cost-effective retrofit model, and
- A costing concept based on this report as well as the follow-up outcome

The outcome of these follow-up investigations will be published in a supplemental report, expected to be presented to the 67th ExCom meeting.

2. Design, Execution

The objectives of this project have been to:

1. Develop, optimize and validate low cost options for hydrocarbons as auxiliary blowing agent in polyurethane foam applications;
2. To demonstrate the technology in downstream applications, and
3. To transfer information collected to interested system houses and downstream users

It should be stated upfront that none of these options should impair safety as currently required. It is referred in this context to international standard IEC 79-10, second edition (1986) and to MLF paper UNEP/Ozl.Pro/ ExCom/25/54, 1998

These safety requirements are summarized in **Attachment-I.**

Technology assessment is a global task. However, it has to be executed in a particular country. UNDP choose Egypt—and the Government of Egypt accepted—for the following reasons:

- HC technology is well established in Egypt
- The center of HC development—Europe—is close
- UNDP has a long tradition in working with the Egyptian foam industry

This project is different from other pilot projects that focus on HCFC replacement technologies in polyurethane foams. In these other projects, the technology to be assessed is a new one, which requires development of formulations for all applications. In the HC case, the base technology exists for quite a while—since around 1992—and has been broadly applied in non-A5 as well as A5 contexts in companies that would meet critical size and technical proficiency. In praxis this meant that a company should use at least 50t/y HCFCs and have adequate in-house engineering capabilities. This would translate in eligibility for a grant of (7.83 x 50,000 =) US$ 391,000 which approximated the costs of such a project. For domestic refrigeration plants, which cost more because of the need of (expensive) retrofit of jigs, a higher threshold was set. This effectively limited the technology to large companies only and led indirectly to wide-spread use of HCFC-141b in smaller and/or less sophisticated enterprises. Recently, the financial threshold has increased by 25% in case a project is based on a low-GWP technology—which is the case with hydrocarbons--but so have equipment costs. Therefore, even with a new threshold, if the cost of hydrocarbon technology is not lowered, SMEs can only fall back on environmentally undesirable HFCs, marginally performing water-based systems or hope that the assessment of new technologies—will provide more satisfactory options.

The use of hydrocarbon technology has not materially changed over the last 20 years. It requires costly pre-blending and metering equipment, an explosion-free production area and elaborate safety procedures. Also, in many countries the make-up of the chemical systems is unchanged while elsewhere significant system optimization has taken place (additives, special polyols, co-blending, ….).

UNDP saw options for cost reduction in the following areas:

- Preblending at supplier level would delete the need for a preblender plus auxiliaries—but cause increase in the system price;
- Direct injection of hydrocarbons would also remove the need for a preblender—but increase the equipment cost;
- Introduction of modern HC blends would allow for lower densities—and lower in this way operating costs.

To test the feasibility of these concepts, the development and commercialization both of stable pre-blends that can be safely transported and the development of a multi-purpose, three-component foam dispenser are required.

The project was designed in four steps:

1. development, optimization and validation/demonstration of premixed, stabilized, modern hydrocarbons systems that can be used directly by foam manufacturers (which means that the blowing agent is incorporated) or used together with direct injection of the blowing agent
2. development of a three component foam dispenser, capable to direct inject hydrocarbons (pentane of cyclopentane blends)
3. placing the three-component dispenser at a suitable facility followed by trials with
    a. direct injection of the blowing agent
    b. using a fully preblended polyol system[1]
4. demonstration of the technology followed by dissemination through an inter-regional workshop

Other PU pilot projects carry a second phase to demonstrate commercial application. In this case, there is no need. The system development part will be an optimization based on knowledge that is already available and incremental success is virtually assured. Building a three component foaming unit has been before applied in an MLF project through retrofit (Turkey, in an ICF project) and will be rather a design optimization than application of a new concept. Also, there is no need to demonstrate the two technology versions in all foam applications. The variations in required formulations are well known to the chemical suppliers that cater to HC systems.

As mentioned before, hydrocarbons are highly flammable. UNDP considers the process at the system house (blending) and at user level (processing) hazardous and requiring adequate safeguards. UNDP requires a safety audit to be conducted prior to commercial operation of a converted plant.

The actual implementation allowed for some consolidation of the four mentioned steps:

1. **Equipment Development –** selected through standard procurement procedures by a qualified equipment supplier selected through standard procurement
2. **System Development –** selected through standard procurement procedures by a qualified system house including t**rials** at a local foam manufacturer or system house that is willing to conduct these and has the capabilitie**s**
3. **Reporting –** This includes an information dissemination inter-regional workshop, followed by a final report to the ExCom on the overall outcome

The bidding process led to the selection of SAIP/Pozzi-Ariozo for both system and equipment development. SAIP/Pozzi suggested—and UNDP accepted—to team up for its system development with Dow Systems, Italy and for trials with Dow Systems, Egypt. This arrangement has worked out very well as will be shown in this report and UNDP wants to express its appreciation to the project collaborators.

For more details on design, related budget, etc., it is referred to the project document in its approved version (**ATTACHMENT-III)**.

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[1] (in addition, HCFC formulations have to be run to establish a baseline for comparison)

3. Outcomes

3.1 General information

Hydrocarbons are clear, colorless liquids with a mild odor. As blowing agent, they are applied in a variety of foams. Pentane isomers are the common choice in polyurethane foams—and from these predominantly cyclopentane (CP) is used. Their main physical properties are as follows (compared to HCFC-141b):

	HCFC-141b	normal-pentane	iso-pentane	cyclo-pentane
Chemical Formula	$C_2H_3Cl_2F$	C_5H_{12}	C_5H_{12}	C_5H_{10}
Molecular Weight	117	72	72	70
Boiling point (^{0}C)	32	36	28	50
Gas Conductivity (mWm^{0}K at 25 ^{0}C)	10.0	14,6	13,8	12,0
Flammable limits (in air by vol. %)	7.6-17.7	1.4-8.3	1.4-8.3	1.4-8.3
GWP (100 y)	0.11	11	11	11
ODP	630	0	0	0

Below is a comparison of cyclopentane with other common foam blowing agents on the most relevant properties:

Property	**HCFC-141b**	**Methylal**	**Cyclo Pentane**	**HFC-245fa**	**Methyl Formate**
LFL/UFL (%)	7.3-16.0	1.6/17.6	1.4-8.0	None	5.0-23.0
Molecular Weight	117	76	70	134	60
Gas Conductivity (mW/m^{o}K)	10 (25^{o}C)	14.5 (42^{o}C)*	11 (10^{o}C)**	12.5 (24^{o}C)	10.7 (25^{0}C)
TLV/OEL (ppm)	500 (TLV)	1,000 (TLV)	600 (TLV)	300 (WHEEL)	100 (TLV)
GWP (100 y; IPCC-1996)	630	Negligible	11	820	Negligible
ODP	0.11	0	0	0	0
MIR* **	<0.01	0.89	2.39	0.00	0.06

* Extrapolation at 25 ^{o}C would be ~ 11;

** Extrapolation at 25 ^{0}C would be ~13.9

*** Photochemical ozone creation potential

Cyclopentane is offered in different purities. Mostly used in foam applications are the commercial grade (70%) and the pure grade (90%). Cyclopentane's toxicity profile compares as follows with HCFC-141b:

	Cyclopentane	HCFC-141b
• TLV (TWA)	600 ppm	500 ppm
• Acute toxicity (oral)	LD50 >5 g/kg (rat)	LD50 5 g/kg (rat)
• Eye irritation:	none	minor to moderate
• Skin irritation:	none	none to slight
• Dermal sensitization:	not allergenic	non allergenic

Hydrocarbon users can for relatively moderate costs (around US$ 1,000/unit) conduct their own compliance testing with a portable electronic monitor.

The Global Harmonization System (GHS) classification for cyclopentane is as follows

Flammable liquids,	Category 2
Specific target organ systemic toxicity - single exposure,	Category 3
Aspiration hazard,	Category 1
Acute aquatic toxicity,	Category 3
Chronic aquatic toxicity,	Category 3

Following flammability related data are available:

- flash point (open cup): -35°C (-31°F)
- auto-ignition temperature: 361°C (682°F)
- flammability limits: 1.4 % vol (LFL)/9.4 % vol (UFL)

Cyclopentane has the following comparable eco-toxicological profile:

	Cyclopentane	**HCFC-141b**
• Daphnids, fish (Brachydanio Rerio)	10.5-100 mg/l	31.2 – 126 mg/l

The USEPA considers all hydrocarbons to be precursors to ground-level ozone, a serious air pollutant in cities across the United States.

Shipment and storage of cyclopentane can be carried out in carbon steel vessels or containers. No special material is required. Carbon steel is also acceptable for storage and piping. Protection from sunlight and avoidance of high ambient temperatures (>30^0C) is required.

Pentanes are not very well miscible with polyols. This might be one of the reasons that system suppliers generally have refrained from offering preblended systems. However, some suppliers, during last 12 years, have tried to minimize the separation issue through improved formulations (noting that such formulations are supplier-specific and may be proprietary). This has led to isolated cases where preblended systems have been offered and continue to be offered in the market. It is estimated that currently 2,000-3,000 t systems are sold preblended in Europe. Sales of preblended systems outside Europe have not been identified. It should be noted that the suppliers of these preblended systems consistently declare such blends according to the GHS system (see before) UN 1993, class 3, product groupie (flammable). Packing is in tightly sealed containers with safety labels (Class 3/UN 1993). Containers are steel or antistatic plastic. UNDP agrees with these classifications and recommends its use for projects based on its assessment.

3.2 Equipment Development and Evaluation

Current HC technology is based on in-house preblending with the polyol blend. SAIP was selected to commission equipment that would be able to operate with preblended (flammable) systems as well as to directly inject (cyclo)pentane into the mixing head ("three component system") without jeopardizing safety. The equipment SAIP delivered consisted of three separate modules:

The isocyanate module in a standard configuration with

- No enclosure and ventilation
- No gas detection system
- No explosion proof components

The polyol module, including the hydrocarbon blend line with

- Enclosure and ventilation
- Drip pan
- Pipes, hoses and fittings leak-free
- Nitrogen blanketing
- Electrical grounding
- Gas sensors
- Explosion proof components
- Magnetic couplings
- Closed loop mixing device

The HC line with

- Enclosure and ventilation
- Drip pan
- Pipes, hoses and fittings leak-free
- Nitrogen blanketing
- Electrical grounding
- Gas sensors
- Explosion proof components
- Magnetic couplings (tank, stirrer)

The mixing head is a self-cleaning laminar flow one three component device with a flexible exhaust line.

The polyol and pentane modules as well as the mixing head meet ATEX 94/9/EC and are in conformity to II 2 Gc IIB T4 as well as the requirements as listed in UNEP/Ozl.Pro/ ExCom/25/54, 1998.

The equipment was installed, commissioned by Dow's internal safety department and functioned well for HCFC systems (baseline), preblended systems and direct injection. In particular, the dispenser offered

- Excellent repeatability
- Acceptable 3 stream blending, although some catalyst adjustments needed to be made
- High efficiency in blowing agent containment, leading to lower densities

UNDP and SAIP have agreed to use the remaining project funds to further optimize the mixing head to achieve even better blending. For details it is referred to the attached report by SAIP (**Attachment-IV**).

3.3 System Development and Evaluation

Along with the contract for a multi-purpose, three-component PU foam dispenser, SAIP/Pozzi Arioso received also a contract for the development and testing of preblended and three component systems. As mentioned, this part of the project was executed in cooperation with the Dow Chemical Company through its international systems development center in Italy in Correggio/Italy and its regional system house in 10th of Ramadan City/Egypt.

Six different systems were selected:

Application Blowing Agent	Commercial Refrigeration	Discontinuous Panels	Water Heaters
HCFC-141b	System A	System C	System E
Cyclopentane (CP)	System B	System D	System f
Normal Pentane (NP)	System B	System D	

The HCFC-141b systems served to provide a baseline while the choice of pentane isomers reflects current market preferences. All pentane blown systems were evaluated as fully formulated systems (blowing agent included and partially blended systems (blowing agent added as a third stream.

All systems were tested on

- Physical and chemical stability of the blends
- System properties of the foams
  (processability, mechanical properties, dimensional stability and thermal properties)

The outcomes of the tests can be summarized as follows:

Blend Stability

The market standard for a fully formulated system is 6 months with an exception for sprayfoam systems, which does not apply to this assessment. Stability is characterized as the blend being homogenous (no phase separation) and substantially unchanged reactivity (free rise density, gel time). Blends based on n-pentane shows phase separation after one month storage and are not anymore suitable for use. Blends based on cyclopentane show after 20 weeks, the duration of the tests, no separation, no density changes and only slightly faster reactivity.

It should be pointed out that separation parameters/conditions beyond the mentioned duration have not been tested, and in different storage and environmental conditions this may result in safety-related challenges. Therefore, precautions should be taken to carefully monitor the quality of the available blends using the help of system houses serving as suppliers to a specific client or with in-house capabilities. Downstream users should follow supplier's recommendations on storage conditions.

For more details it is referred to **Attachment-VI**.

System Properties

Processability has been compared with HCFC-141b and between preblended and directly injected cyclopentane. In all cases commercially usable systems have been obtained.

Commercial Refrigeration

The market uses no n-pentane. Compared with HCFC-141b cyclopentane shows:

- A larger temperature window

- Higher reactivity
- Lower free and applied density
- Lower compressive strength (density related)
- Higher k-factors
- Better adhesion
- Equal dimensional stability
- Lower post-expansion (better cycle time)

The lower compressive strength is still within the parameters of acceptability.

Comparing preblended versus directly injected hydrocarbons, direct injection shows

- Similar reactivity
- Lower free density (applied density equal as per design)
- Lower compressive strength (density related?)
- Equal k-factors
- Lower adhesion (still better than with HCFCs)
- Slightly lower post-expansion

The study was not designed to investigate the option to lower applied density ; this could remain an area for further study.

Discontinuous Panels

The market uses n-pentane and cyclopentane.

Compared with HCFC-141b cyclopentane shows

- Higher reactivity
- Lower free and applied density
- Slightly lower compressive strength
- Higher k-factors
- Slightly lower adhesion
- Equal dimensional stability
- Lower post-expansion (better cycle time)

Compared with HCFC-141b n-pentane shows

- Much higher reactivity
- Lower free and applied density
- Lower compressive strength
- Considerably higher k-factors
- Similar adhesion
- Equal dimensional stability
- Much lower post-expansion (better cycle time)

Comparing preblended versus directly injected n-pentane direct injection shows

- Slightly higher reactivity
- Slightly higher free density
- Equal compressive strength (density related?)
- Equal k-factors
- Lower adhesion
- Slightly higher post-expansion

The differences between preblending and direct injection are in this case minor and within the variability ranges of the test methods.

Comparing n-pentane vs. c-pentane comparison shows for n-pentane

- Improved flow properties which can lead to lower applied density
- Improved mechanical properties and dimensional stability
- Improved cycle time properties
- Worse k-factor

Water Heaters

The market uses no n-pentane. Compared with HCFC-141b cyclopentane shows

- Higher reactivity
- Lower free and applied density
- Lower compressive strength
- Higher k-factors
- Lesser adhesion
- Equal dimensional stability

Comparing preblended versus directly injected hydrocarbons, direct injection shows

- Similar reactivity
- similar free density (applied density equal as per design)
- Lower compressive strength
- Equal k-factors
- Same adhesion

The differences between preblending and direct injection are in this case also minor and within the variability ranges of the test methods.

For more information it is referred to **Attachments IV and V** that contain the Dow laboratory reports and provide detailed descriptions of the experiments conducted as well as the results achieved.

4. Conclusions

4.1 Pre-blended Cyclo-pentane

- Pre-blended cyclopentane systems are sufficiently stable and can be commercially used with application of applicable safety measures. It is recognized, however, that the shelf life will also be dependent on a specific formulation of a system, therefore needs to be checked for each individual system, and that supplier's storage and safety recommendations need to be followed;
- As no preblender along with its auxiliary equipment (tanks, piping, etc) is needed, cost savings of around US$ 100,000 can be expected;
- Based on lower comparable (to HCFC-141b) free rise densities, incremental operational costs savings of 5.6 % (water heaters) and 7.9 % (commercial refrigeration) can be expected up and above the customary difference based on the price of cyclopentane compared to HCFC-141b. However, more research is needed to confirm this. If confirmed, the overall difference in operating costs is estimated between 6 and 8%. Against this, the possibility of higher transportation costs needs to be considered. UNDP has contacted several suppliers with a request for transportation information but not yet received responses;
- K values are 5-8% higher than for HCFC-141b foams but equal to conventional CP foams.

4.2 Pre-blended Normal-pentane

- Preblended normal-pentane systems are stable for less than a month and therefore not recommended for commercial use.

4.3 Directly injected Hydrocarbons

- In this case normal-pentane as well as cyclo-pentane can be used;
- Equipment developed for this purpose shows good reproducibility and consistency as well as homogenous mixtures, despite higher polyol viscosities;
- However, the k-factor in case of normal-pentane is more than 11% higher than for HCFC-141b formulations, making its use in very critical formulations such as refrigeration and other appliances anyway undesirable;
- Slightly higher k-factor and lower reactivity show that the mixer head impingement has suffered from the introduction of a third stream. While improvement could be made with an optimized catalyst package, redesign of the mixing head should be considered as well;
- Because of minimized blowing agent losses, free blown densities are even lower than for preblended cyclopentane;
- No preblender along with auxiliary equipment (tanks, piping, etc) is needed but the need for a third dosing line might absorb most, if not all of these savings;
- Based on lower comparable densities, incremental operational costs savings of up to 10% can be expected up and above the customary difference based on the price of cyclopentane compared to HCFC-141b. The overall difference in operating costs is estimated to be up to 10%. No additional transportation costs will apply in this case. This statement still needs, as mentioned before, confirmative trials.

While all technical statements are considered universally valid, cost statements are valid in the Egyptian context only and would need to be adjusted in other regions.

ATTACHMENTS

ATTACHMENT I:

PROCESS SAFETY GUIDELINES

IN THE MANUFACTURE OF PU INSULATION FOAMS WHEN USING FLAMMABLE SUBSTANCES AS BLOWING AGENT

The following safety concept is based on internationally recognized and applied standards. In addition, it is possible that local standards or company policies exist that have to be adhered to. The stricter one will prevail in a given situation.

- **Classify all identified hazard areas following IEC 79-10, second edition, 1986:**

  Zone 0: **Where a constant amount of highly flammable/ explosive liquids or gases may be expected. Material must be explosion- proof and grounded.**

  Zone 1: **Where, from time to time, highly flammable liquids or gases may be expected. Material must be Ex-e, -d or -i and grounded.**

  Zone 2: **Where only by accident or scheduled maintenance highly flammable/explosive gases may be expected. Material required is Ex-n or with IP54 sealing. Grounding is required.**

- **Reclassify or restrict as many areas as possible by the application of engineered solutions such as ventilation, ionized air blowers, other static dissipaters, separation walls, etc.;**

- **Safeguard areas that cannot be reclassified, through explosion proofing;**

- **Provide additional safeguarding through the use of a combustible gas monitoring system with sensors at designated potential emission points and a portable gas detector to be used as part of a formal monitoring plan for areas that do not have continuous monitoring;**

- **Provide adequate emergency response gear such as firefighting equipment;**

- **Train personnel in safe operating procedures, preventive maintenance, and emergency response. Use formalized procedures through the preparation of a safety manual and an emergency response plan;**

- **Use an external expert or a technology transfer agreement to supervise all designs, the implementation and the start-up. The initial production start-up after conversion should be attended by experienced operating personnel.**

With the help of this safety concept, it is possible to design actual modifications that have to be made to implement the transfer from CFCs to hydrocarbons. Actual implementation can differ, depending on equipment, plant layout, housekeeping and surroundings.

A "standard" conversion for a discontinuous process would be along the following lines:

CENTRAL SAFETY AND CONTROL SYSTEMS

Gas Sensing and Alarm System

- The plant shall have installed gas sensors on locations where the possibility of emissions or leakage of CP exist. The sensors are to be connected to a centralized control panel in a safe area, clear from potential emission sources.
- The system shall be capable to trigger two consecutive visual/acoustical alarm levels, related to the percentage LEL reached. Recommended is a first level alarm on 15% LEL and a second alarm level at 30% LEL.
- The acoustical alarm shall be a minimum of 85 Db, or at least 15 Db over plant noise level.
- The visual alarm shall be in the pouring area.
- The first alarm shall be for warning purposes only.
- The second alarm shall shut down the pouring operation and the pentane supply, while increasing the process exhaust.
- The system shall have an independent power back-up.
- An auxiliary portable gas sensor with calibration unit shall be kept on site.

Exhaust System

- The plant shall have installed a centralized or sufficient localized emission extraction systems of sufficient capacity serving locations where the possibility of emissions or leakage of pentane exists.
- The system(s) shall have a two stage capacity and back-up power.
- The system(s) shall be interlocked with the sensor and alarm system.
- The system(s) shall have an independent power back-up.

Grounding

- All equipment in areas where CP emissions or leakage can occur shall be connected to a central electrical grounding system.
- The grounding shall conform to internationally accepted specifications e.g. NFPA 77.

Procedures

- The enterprise shall provide the necessary operational safety and emergency response instruction and training to staff and personnel involved in the operations using cyclopentane.
- A Safety Manager shall be appointed in the factory. The manager will receiver appropriate training and education and be properly certified.
- Hazardous areas shall be clearly marked by signs indicating the Area Zoning.
- Piping shall be color coded.
- No smoking shall be allowed in the factory and its immediate surroundings. The no smoking policy shall be properly marked by signs.
- Periodic safety audits shall be effected. The audits shall include measuring of CP concentrations in areas not covered by permanent sensors through the use of the portable sensor by a qualified person.
- A Safety Manual shall be developed and maintained. The manual should as a minimum address:
    - Safety Organization and Responsibilities
    - Standard Procedures for Work in Hazardous Areas
    - Response to Emergency Alarms
    - Start-up procedures after Emergency Shutdown

CYCLOPENTANE STORAGE AND TRANSFER

- Location and installation of storage systems for hydrocarbons are subject to local regulations..
- Design of tank, piping, valves shall comply with internationally recognized standards, e.g. ISPEL, NFPA 30 and NFPA 58. Recommended design pressure for a HC container is 250 psi.
- Tanks shall have an electrically/pneumatically operated shutoff control valve on the outlet pipe of the tank that can be activated from within the plant. In addition, it shall be possible to shutoff the electrical power supply to the tank from within the plant as well as at the tank.
- Nitrogen blanketing shall be provided.
- All components shall be properly grounded.
- Protection against lightning may be required depending on location.
- All installations within 4 m radius of the tank shall meet Zone 1 requirements.
- Minimal one gas detector, connected to the central gas sensing and alarm system, shall be installed.
- At a minimum two portable fire Extinguishers shall be installed.
- The tank shall be in a concrete (spill) containment of sufficient size in a fenced, locked area, preferable with a cover to protect against direct sunlight.
- The CP transfer pump, if included, shall be explosion proof with backflow protection.

PREBLENDER

- The preblender shall be placed in/on a spill containment of sufficient size.
- It shall be placed in an enclosure, connected to an adequately sized two stage air extraction system that allows 6/10 air replacements/hour.
- One gas detector shall be installed, attached to the central gas sensing and alarm system.
- The preblender shall be connected to a polyol buffer tank through a pump with backflow protection and to the CP storage and transfer system through an explosion proof pump with backflow protection.
- All equipment inside the enclosure shall meet Zone 1 requirements.
- All equipment shall be properly grounded.

FOAM DISPENSER

- Tanks shall be placed in/on individual spill containment of sufficient size.
- At a minimum, the polyol tank and pump shall be placed in an enclosure, attached to an adequately sized two stage ventilation system that allows 6/10 air replacements/ hour. Placement of the complete dispenser in an enclosure is recommended.
- Drip pans shall be placed under metering pumps.
- All installations in the enclosure shall meet Zone 1 requirements.
- At a minimum one gas detector shall be installed, attached to a central gas sensing and alarm system.
- Minimal two 6 kg ABC portable fire extinguishers shall be installed close to the foam dispenser.
- All equipment shall be properly grounded.

MOLDS, FIXTURES, PRESSES

- Cavities in closed molds, fixtures and presses shall be inerted by nitrogen prior to the foam pouring operation. IEC 79-10 provides instructions for the calculation of the amount of inertization gas.
- Emissions from molds, fixtures and presses shall be removed through an adequately sized two staged extraction system. Calculation of the lower stage ventilation capacity should be based on the emission of 5% of the CP injected.
- Generation of static electricity should be minimized through proper grounding. In addition, the installation of ionized air blowers is recommended.

SAFETY INSPECTION CHECKLIST

Prepared by: **For:**

Date: **Project:**

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1. CYCLOPENTANE STORAGE AND TRANSFER

REQUIREMENTS		OK	COMMENTS /ACTIONS
1.1	Meets local Specifications		
1.2	Certified by recognized Institution		
1.3	Suitable located		
1.4	Protected against traffic		
1.5	Placed on a pavement		
1.6	Fenced in with locked door		
1.7	Spill basin of adequate size		
1.8	Electrical installation meeting codes		
1.9	Gas sensor installed and operational		
1.10	Nitrogen blanketing		
1.11	Leak detection installed (Only required for underground tanks)		
1.12	Two 9 kg ABC fire extinguishers		
1.13	Connection to the premixer meeting requirements		
1.14	Grounded, with extra cable to connect to drums or tank truck		
1.15	Interconnected with the central safety/alarm system (automatic shut-off valve, gas sensor)		
1.16	Water hydrant in vicinity		
1.17	Easy access for delivery /operation		
1.18	Ex transfer pump with backflow protection and lubrication		

2. POLYOL/PENTANE PREBLENDER

REQUIREMENTS		OK	COMMENTS /ACTIONS
2.1	Placed in a spill containment		
2.2	Placed in an enclosure attached to a two speed exhaust system		
2.3	Gas sensor installed and operational		
2.4	Connected to a polyol service tank with backflow protection		
2.5	Polyol service tank placed in a spill containment of 110%		
2.6	Electrical installation meeting codes		
2.7	One 6 kg ABC fire extinguisher in the direct vicinity		
2.8	Connected to an electrical grounding system		
2.9	Interconnected with the central safety/alarm system (ventilation and gas sensor)		

3. FOAM DISPENSING AREA

REQUIREMENTS		OK	COMMENTS /ACTIONS
3.1	Tanks placed in separate spill containments of 110% each		
3.2	Drip pans under pumps		
3.3	Polyol tank and pump placed in an enclosure attached to a two speed exhaust system		
3.4	Electrical installation meeting codes		
3.5	Two gas sensors installed and operational		
3.6	Connected to an electrical grounding system		
3.7	Two 6 kg ABC fire extinguisher in the direct vicinity		
3.8	Nitrogen blanketing polyol tank		

3.9 No cavities in the floor		
3.10 Interconnected with the central safety/alarm system (ventilation, automatic shut-off, gas sensor)		
3.11 Separated from other operations		

4. POURING AREA (INCLUDING MOLDS AND FIXTURES)

REQUIREMENTS	OK	COMMENTS /ACTIONS
4.1 Installed in a separate area		
4.2 No cavities in the floor		
4.3 Explosion proof electrical fixtures		
4.4 Connected to a two speed exhaust system of sufficient capacity		
4.5 Gas sensors installed/operational at each pouring location		
4.6 Installation of a nitrogen flushing system on the mixing heads		
4.7 Installation of a nitrogen inertization system for the molds/fixtures		
4.8 Electrical installation meeting codes		
4.9 A 6 kg ABC fire extinguisher placed at each mold/fixture		
4.10 Mixheads, fixtures, molds connected to an electrical grounding system		
4.11 Interconnected with the central safety/alarm system (ventilation and gas sensors)		

5. CENTRAL SAFETY/ALARM SYSTEM

REQUIREMENTS	OK	COMMENTS /ACTIONS
5.1 Placed in a safe, accessible area, separated from hazardous operations		
5.2 Interconnecting all gas sensors, exhaust systems, shut-off valves and any other emergency features into one central management system		

5.3 Capable to trigger alarm on two consecutive LEL percentages		
5.4 Featuring acoustical as well as visual alarm and process shut down		
5.5 Independent power back-up		

6. SAFETY MANAGEMENT PROCEDURES

REQUIREMENTS	OK	COMMENTS /ACTIONS
6.1 Provision of operational safety and emergency response instruction		
6.2 Appointment of a Safety Manager		
6.3 Marking of all hazardous area's by signs indicating the area coding		
6.4 Installation of non-smoking signs		
6.5 Color coding of piping		
6.6 Institution of pertinent standard operational procedures to assure proper safety		
6.7 Handheld sensor/calibrator		
6.8 Institution of regular safety audits, including measurements with the Handheld sensor		
6.9 Emergency response planning		

ATTACHMENT II:

HCFC PHASEOUT TECHNOLOGIES IN PU FOAM APPLICATIONS

Francesca Pignagnoli
Bert Veenendaal

July 4, 2011

1. INTRODUCTION

HCFCs are currently still in use in developing ("A2") countries as blowing agents in polyurethane (PU) foams. To replace these HCFCs, following criteria would ideally apply:

- A suitable boiling point with 25^{0}C being the target,
- Low thermal conductivity in the vapor phase,
- Non flammable,
- Low toxicity,
- Zero ODP,
- Low GWP,
- Chemically/physically stable,
- Soluble in the formulation,
- Low diffusion rate,
- Based on validated technology,
- Commercially available,
- Acceptable in processing, and
- Economically viable.

CFC phaseout in rigid and integral skin foams has been mostly achieved by replacement through

- Hydrochlorofluorocarbons (HCFCs)
- Hydrocarbons (HCs)
- Carbon dioxide (CO_2), generated from water/isocyanate or applied directly as liquid or gas

HCFCs, in turn, have already been replaced in many developed countries by hydrofluorocarbons or HFCs. At the same time, suppliers are looking to reduce flammability and other safety-related issues as well as environmental impact. In particular, achieving low GWPs is emerging as an important condition for acceptability of HCFC replacements. Following table provides an overview of currently available or emerging HCFC alternatives. Following indicative GWP changes are to be expected for available or emerging replacements of HCFC-141b in PU foam applications:

SUBSTANCE	GWP[1]	MOLECULAR WEIGHT	INCREMENTAL GWP[2]	COMMENTS
HCFC-141b	725	117	Baseline	
CO_2	1	44	-725	Used direct/indirect (from water)
Cyclopentane	11[2]	72	-718	Extremely flammable
HFC-245fa	***1,030***	***134***	***443***	
HFC-365mfc	***794***	***148***	***279***	
HFC-134a	***1,430***	***102***	***522***	
Methyl formate	negligible	60	-725	
Methylal	negligible	76	-725	
Acetone	negligible	58	-725	Used in flexible slabstock
FEA-1100	5	164[4]	-718	Under development

HFO-1234ze	6	114	-719	Recently introduced
HBA-2	<15	<134	>-708	Under development
AFA-L1	<15	<134	>-708	Under development

[1] Unless otherwise indicated, taken from IPCC's Fourth Assessment (2007)

[2] Derived from comparing GWPs compared to the baseline on an equimolar base. It should be noted that in practice formulators may make
changes such as increased water or ABA blends that impact the global warming effect

[3] From UNEP Foams Technical Options Committee's 2006 report

[4] Calculated from published formulations

Green = beneficial GWP effect; ***red* = unfavorable GWP effect**

These technologies are described in more detail below. It should be pointed out that a comparison between GWP is an approximation of the climate effect. A full lifecycle determination or a functional unit approach (as described by the MLF Secretariat in it paper 55/47) which includes energy efficiency and other factors is a better—but more lengthy —approach.

1. PROVEN ZERO ODP TECHNOLOGIES

HYDROCARBONS

Pentane isomers are the most utilized hydrocarbon blowing agents (Bas). Their main physical properties are as follows:

	normal-pentane	iso-pentane	cyclo-pentane
Chemical Formula	C_5H_{12}	C_5H_{12}	C_5H_{10}
Molecular Weight	72	72	70
Boiling point (^{0}C)	36	28	50
Gas Conductivity (mWm^{0}K at 25 ^{0}C)	14,6	13,8	12,0
Flammable limits in Air (vol. %)	1.4-8.3	1.4-8.3	1.4-8.3
GWP (100 y)	11	11	11
ODP	0	0	0

Hydrocarbons are Zero ODP/Low GWP flammable blowing agents and are a preferred solution for those producers who can afford the investment for managing safe handling of flammable formulations. Evolution of hydrocarbon formulations has come to the point that systems can meet fire behavior requirements despite the flammability of the BA. Among the different isomers available, n-pentane or the commercial blends of n-pentane and iso-pentane are the most cost effective ones and are used in construction application, mainly through continuous production process.

On the other hand, c-pentane is more soluble than n-pentane or iso-pentane and features the lowest thermal conductivity within the family of isomers. Because of this, it is a preferred choice for those applications where thermal conductivity is a key property, for instance domestic appliance and commercial refrigeration industry. Fine tuning of properties has taken place as well through blends (like cyclo-pentane/isopentane or cyclo-pentane/iso-butane, where iso-butane is a gaseous molecule with limited solubility, its use is not wide-spread).

There have been many HC-based/MLF-supported CFC-phaseout projects in refrigeration and in panel applications. The technology, however, was deemed unsafe for applications such as spray and in situ foams ("PIP"). Despite that these blowing agents are low cost molecules, the investment costs to handle their flammability aspects are the same as at the time of phasing out CFCs and the technology will continue to be too expensive for SMEs and restricted in principle to the same applications as before.

However, there are options to fine-tune project costs and investigate other applications:

- The introduction of HC blends that will allow lower densities (lower IOCs)
- Direct injection (lower investment)
- Low-pressure/direct injection (lower investment)
- Centralized pre-blending by system houses (lower investment for foam manufacturer)
- Application-specific dispensing equipments

UNDP has initiated a study some of these options in Egypt.

HYDROFLUOROCARBONS (HFCs)

There are currently three HFCs used in foam applications. Their main physical properties are as follows:

	HFC-134a	HFC-245fa	HFC-365mfc
Chemical Formula	CH_2FCF_3	$CF_3CH_2CHF_2$	$CF_3CH_2CF_2CH_3$
Molecular Weight	102	134	148
Boiling point (^{0}C)	-26.2	15.3	40.2
Gas Conductivity (mWm^{0}K at 25 ^{0}C)	14,3	12.2	10.6
Flammable limits in Air (vol. %)	None	None	3.6-13.3
TLV or OEL (ppm; USA)	1,000	300	Not established
GWP (100 y)	1,410	1,020	782
ODP	0	0	0

Hydrofluorocarbons are non flammable blowing agents, when considering that the only one which shows flammability limits, HFC365mfc, is commercialized as non flammable blend of HFC-365mfc/227ea.

Gaseous HFC-134a has limited solubility into formulated polyols and concentrations above the solubility limit requires pressurized equipment or the addition of the BA directly in the mixing head of the machine (e.g. in case of continuous production DBL) or in the high pressure polyol stream via a static mixer (in case of discontinuous production). Combination of HFC-134a with liquid HFCs (HFC-245fa and/or the non flammable blend HFC-365mfc/227ea) are often practiced in order to decrease applied density and improve thermal conductivity versus the use of HFC-134a alone, reducing cost of solutions containing high levels of liquid HFCs alone, as they are more expensive than gaseous ones.

HFC-245fa is a non flammable BA and its boiling point allows the handling as a liquid under moderate pressure, but attention has to be put to overall vapor pressure in blends where high levels are used.

In general , the availability of "low level" solutions addresses the need to find the best cost/performance balance at reduced GWP impact, while the use of HFC 245fa and HFC 365/227 at high levels, allows to obtain excellent foam insulation and processing performance.

Current HFC use in A5 countries is a niche application. There is some use of HFC-134a in shoe soles—most notable in Mexico. Apart from the price, the use is complicated because of its low boiling point. The use of other HFCs is limited mainly to products for export—and even then sporadic. On the other hand, these chemicals have played a major role in the replacement of HCFCs in foam applications in non-A5 countries—despite high GWP potentials.

Generally, the use of water has been maximized and sometimes other co-blowing agents have been added. High water / low HFC level technologies, which mitigate the HFCs GWP impact, can help producers to bridge time till new Zero ODP and low GWP blowing agents like HFOs will be available.

CARBON DIOXIDE

	Carbon dioxide
Chemical Formula	CO_2
Molecular Weight	44
Boiling point (^{0}C)	-78
Gas Conductivity (mWm^{0}K at 25 ^{0}C)	16,3
Flammable limits in Air (vol. %)	none
TLV or OEL (ppm; USA)	
GWP (100 y)	1
ODP	0

Carbon dioxide can be applied as a blowing agent through water, through formic acid and directly.

- **AS WATER**

The use of carbon dioxide derived from the water/isocyanate chemical reaction is well researched. It is used as co-blowing agent in almost all PU foam applications and as sole blowing agent in foam applications that have no or minor thermal insulation requirements.

Full water blown technology is Zero ODP, it has the lowest GWP and, differently from HC based solutions, it is non flammable and can be easily implemented with no/small capital investment.

For this reason, increased use of water/CO_2 has been and still is an important tool in the HCFC phaseout in cases where HCs or other blowing agent technologies cannot be used for economic or technical reasons.

The successful development of water blown foams has been a real challenge due to its intrinsic physical hurdles such as higher thermal conductivity, lower foam dimensional stability - which generally requires to increase the applied density –, and higher surface brittleness, resulting in a potentially weaker adhesion to metal facings. Formulated polyol viscosity and reaction exothermicity are inherently higher due to the absence of a physical BA like HFCs or pentane with consequent impact on its processability. Despite these hurdles, some formulation suppliers succeeded in developing specific water blown technologies for commercial refrigeration applications, including sandwich panels and commercial appliances.

Ultimate generation fully water blown solutions can be adopted to address environmental call without entering into significant equipment changes investments, leaving the opening to be converted later on into co-blowing with physical blowing agents by the time when new proven low ODP low GWP non flammable solutions will be available.

Recent development activities, mainly focused on the commercial appliance industry, have resulted in the development of new water blown technology characterized by greatly improved performance that can now be considered in line with HFC low level technologies. Typical initial thermal conductivity is in the range of 22–23 mW/mK (measured at 10°C), relatively higher compared to pentane and/or some HFCs blown solutions. Nevertheless, water blown technology is mainly used for the insulation of commercial appliances whenever the foam thermal conductivity requirements are less stringent (for instance for display cabinets where the heat-flow through the foam brings only a limited contribution to the equipment energy consumption).

- **AS FORMIC ACID**

The addition of formic acid as chemical blowing agent can provide technical advantages compared to full water-blown technology. They provide excellent foam aesthetics, improved processability and good performance (in terms of flow, density distribution and adhesion), in particular at low mold temperature. Nevertheless some drawbacks have been identified and need to be taken in consideration. They are mainly linked to potential corrosion issues, which requires the machine manufacturers' involvement in order to check and to improve the equipment suitability. Despite this hurdle, some formulators succeeded in developing specific water/formic acid blown technology featuring high and consistent performance in defined time window frame, provided storage conditions are respected.

The technology is mainly in use today in the market as an non-ODP/low GWP way to optimize the performance of full water blown technology, in applications where enhanced flow, lower density and outstanding aesthetics are key requirements, i.e. the production of sandwich panels for cold store applications.

Use of formic acid technology requires pre-risk assessment with equipment suppliers and adoption of suitable dispensing unit parts, like pumps & nozzles, to handle it, in order to prevent potential metal corrosion issues.

- **DIRECTLY**

Carbon dioxide can also be added as a physical blowing agent. This is mostly the case in flexible foam and therefore not an HCFC replacement. However, there is also use of super-critical CO_2 in sprayfoam applications in Japan. UNDP is conducting a pilot project to assess the merit of this technology.

2. EMERGING TECHNOLOGIES

METHYL FORMATE (MF or ECOMATE®)

Property	**Methyl Formate**	**HCFC-141b**
Appearance	Clear liquid	Clear liquid
Boiling point	31.3 °C	32 °C
LEL/UEL	5-23 %	7.6-17.7
Vapor pressure	586 mm Hg @ 25 °C	593 mm Hg @ 25 °C
Lambda, gas	10.7 mW/m.k @ 25 °C	10.0 mW/m.k @ 25 °C
Auto ignition	>450 °C	>200 °C
Specific gravity	0.982	1.24
Molecular weight	60	117
ODP	0	0.11
GWP	Negligible	630
TLV (USA)	100 ppm TWA/150 ppm STEL	500 ppm TWA/500 ppm STEL

Methyl-formate, also called methyl-methanoate, is a low molecular weight, flammable chemical substance. Its MSDS mentions R12 (extremely flammable but not explosive); R20/22 (harmful by inhalation and if swallowed) and R36/37 (irritating to eyes and respiratory system). Foam Supplies, Inc. (FSI) in Earth City, MO has commercialized its use as a blowing agent in PU foams from 2005 onwards. The application has been patented in several countries.

In December 2010, the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol, short MLF, cleared the use of this substance in MLF projects. Ecomate®, as FSI calls the product, has been initially licensed exclusively to selected distributors but MLF system house clients can receive non-exclusive licenses. The decision was based on an assessment prepared by UNDP that resulted in the following recommendations:

- To allow the use of Methyl Formate as an alternative blowing agent to HCFC-141b in PU foam applications in MLF projects
- To implement such projects preferably through system houses
- To adhere to local regulations on industrial hygiene and fire safety
- For project designers to ensure that:
  - Chemical compatibility is verified
  - Minimum density is observed
  - Health, safety and environmental recommendations are incorporated
  - Implications related to acidity are taken into account

Because of inhalation and flammability concerns, UNDP commissioned an industrial hygiene study in Brazil under “worst case scenarios” (open blending and sprayfoam operations) which showed process emissions to be well below 100 ppm, (STEL). 100 ppm equals 0.2% LFL, so that meeting IH conditions.

MF is normally sold as a system, which, with proper choice of polyols and additives, would restrict flammability issues to the supplier.

METHYLAL

Property	**Methylal**	**HCFC-141b**
Appearance	Clear liquid	Clear liquid
Boiling point	42 ^{o}C	32 ^{o}C
LEL/UEL	2.2-19.9 %	7.6-17.7
Vapor pressure	400 mm Hg @ 20 ^{o}C	593 mm Hg @ 25 ^{o}C
Lambda, gas	Not available	10.0 mW/m.k @ 25 ^{o}C
Auto ignition	235 ^{o}C	>200 ^{o}C
Specific gravity	0.821 @ 20 ^{o}C	1.24
Molecular weight	76.09	117
GWP	Negligible	630
TLV (USA)	1000 ppm TWA	500 ppm TWA/500 ppm STEL

Methylal, also called dimethoxymethane, belongs to the acetyl family. It is a clear colorless, chloroform-like odor, flammable liquid with a relatively low boiling point. Its primary uses are as a solvent and in the manufacture of perfumes, resins, adhesives, paint strippers and protective coatings. It is soluble in three parts water and miscible with the most common organic solvents.

The use of Methylal as a co-blowing agent in conjunction with hydrocarbons and HFCs for rigid foam applications (domestic refrigeration, panels, pipe insulation and spray) has been described in the literature. It is claimed that Methylal improves the miscibility of pentane, promotes blending in the mixing head, foam uniformity, flow, adhesion to metal surfaces and insulation properties, reducing simultaneously the size of the cells.

Despite all literature references, public knowledge of Methylal's industrial performance as blowing agent is quite limited. To validate its use as a possible replacement of HCFCs for MLF projects in developing countries, UNDP has conducted in Brazil and Mexico assessments. While it has already shown good performance, the flammability of systems containing >3 php is a concern and may restrict its use.

3. TECHNOLOGIES UNDER DEVELOPMENT

HYDROFLUOROOLEFINS

	HFO-1234ze	**HBA-2**	**FEA-1100**	**AFA-L1**
Chemical Formula	$CHF=CHF_3$	n/k	n/k	n/k
Molecular Weight	114	<134	161-165 (estimated)	<134
Boiling point (^{0}C)	-19	>15 <32	>25	>10 <30
Gas Conductivity (mWm^{0}K at 10 ^{0}C)	13	n/k	10.7	10
Flammable limits in Air (vol. %)	None	None	None	None
TLV or OEL (ppm; USA)	1,000 (proposed)	n/k	n/k	n/k
GWP (100 y)	6	<15	5	Negligible
ODP	0	0	0	0

Since early 2008, several new blowing agents for PU foams have been proposed by major international manufacturers of halogenated compounds. Four of them are worth mentioning. These are all geared towards replacement of HFCs and sometimes called "second generation" HFCs, although HFOs appear to have a more distinctive description. They share low/no flammability, zero ODP and insignificant GWPs:

Except HFO-1234ze, all other chemicals listed out in the table above will not be commercialized in the next few years and, most likely, will then first be geared towards developed countries where legal limitations on HFCs are considered. It may appear somewhat late in an A5 context where foam conversion is prioritized. As to HFO-1234ze, this is already in use as a replacement of HFC-134a in one component foams (OCF). There are only few OCF manufacturers in developing countries.

ATTACHEMENT III:
Project on Validation/Demonstration of Low Cost Options for the Use of Hydrocarbons as foaming agent in the Manufacture of PU Foams

COUNTRY:	Egypt
IMPLEMENTING AGENCY:	UNDP
PROJECT TITLE:	Validation/Demonstration of Low Cost Options for the Use of Hydrocarbons as foaming agent in the Manufacture of PU Foams
PROJECT IN CURRENT BUSINESS PLAN:	Based on ExCom Decision 55/43(e i-iii)
SECTOR:	Foams
Sub-Sector:	Rigid and Integral Skin PU Foams
ODS USE IN SECTOR	
Baseline:	Not yet determined
Current (2007):	433 ODP t HCFCs as per Government reporting
BASELINE ODS USE:	n/a (pilot project)
PROJECT IMPACT (ODP targeted):	n/a (pilot project)
PROJECT DURATION:	8 months
PROJECT COSTS:	US$ 473,000
LOCAL OWNERSHIP:	100 %
EXPORT COMPONENT:	0 %
REQUESTED MLF GRANT:	US$ 473,000
IMPLEMENTING AGENCY SUPPORT COST:	US$ 35,475 (7.5 %)
TOTAL COST OF PROJECT TO MLF:	US$ 508,475
COST-EFFECTIVENESS:	11.8 US$/kg-ODS
PROJECT MONITORING MILESTONES:	Included
NTL. COORDINATING AGENCY:	Egypt Environmental Affairs Agency (EEAA) National Ozone Unit

Project Summary

Egypt is a Party to the Vienna Convention and the Montreal Protocol. It also ratified the London, Copenhagen and Montreal amendments. The country is fully committed to the phaseout of HCFCs and willing to take the lead in assessing and implementing new HCFC phaseout technologies, particularly in the foam sector—as it did for CFCs in 1992 when it submitted and completed the first foam sector investment projects ever under the MLF. Egypt has local PU system houses that frequently combine importations and distributions for major international chemical and equipment manufacturers with local blending for SMEs. In addition, most international PU chemicals suppliers are represented with offices or their own system houses.

The objective of this project is to develop, optimize, validate and disseminate low-cost systems for the use of hydrocarbons in the manufacture of PU rigid insulation and integral skin foams.

IMPACT OF PROJECT ON COUNTRY'S MONTREAL PROTOCOL OBLIGATIONS

This project is a pilot project aimed to validate optimized HC technology and will contribute indirectly to the fulfillment of Egypt's Montreal Protocol obligations. If successfully validated, the optimized technology will contribute to availability of cost-effective options that are urgently needed to implement HCFC phase-out, particularly at SMEs.

Prepared by: Rappa, Inc. **Date: May 2009**

PROJECT OF THE GOVERNMENT OF EGYPT

PILOT PROJECT FOR THE VALIDATION/DEMONSTRATION OF LOW COST OPTIONS FOR HYDROCARBONS AS FOAMING AGENT IN THE MANUFACTURE OF PU FOAMS

1. PROJECT OBJECTIVES

The objectives of this project are to:

4. Develop, optimize and validate low cost options for hydrocarbons as auxiliary blowing agent in polyurethane foam applications; then
5. demonstrate the validated technology in a representative amount of downstream operations, and
6. transfer the technology to interested system houses and other users

2. INTRODUCTION

Current *validated* technologies for replacing HCFC-141b in foams are restricted to water/isocyanate, hydrocarbons and HFCs. With water non-performing in thermal insulation applications, HFCs being high in GWP and hydrocarbons high in investment costs, it is important that, along with the investigation of other, recently developed, but not yet validated options, these technologies will be investigated on approaches to improve their technical, cost and/or environmental performance. ExCom Decision 55/43 reflects this by promoting pilot projects aimed to validate technologies, mentioning specifically the use of low-cost hydrocarbon technologies. UNDP has followed recent developments in the foam industry closely and prepared four pilot projects which, it believes, cover all commercially available products that have potential—or have been proven—as blowing agent in foams but need optimization/validation/demonstration in an A5 context. These technologies are:

Substance	Sub-Sector	Status	Comments
Hydrocarbons	RPF, ISF	to 58th ExCom	Validation/Demonstration of cost saving options
Methyl formate	RPF, ISF, FPF	Approved	Technical validation of a commercial available product
Methylal	RPF, ISF, FPF	to 58th ExCom	Technical validation of a commercial available product
HFO-1234ze	XPS	to 58th ExCom	Technical validation of a commercial available product

This project covers the validation of low cost hydrocarbon technologies. Technology validation is a global task. However, it has to be executed in a particular country and UNDP is therefore preparing the proposals in consultation and with the consent of the relevant countries, and an endorsement letter from the country is included. However, because of the global impact, deduction of the first phase, which deals with development, optimization and validation from the national aggregate HCFC consumption, would not be fair and it is requested to treat phase-1 this way.

3. PROJECT DESCRIPTION

3.1 PROJECT DESIGN

This project is different from other pilot projects concerning HCFC replacements in polyurethane foams. In other projects the technology to be validated is a new one, which requires development of formulations for all applications. In this case the technology is already existing for quite a while—since around 1992—and broadly applied in an A5 context in companies that would meet a critical size and technical proficiency. In praxis this meant that a company should use at least 50t and have in-house engineering capabilities to be eligible.

This would translate in eligibility for a grant of (7.83 x 50,000 =) US$ 391,000 which approximated the costs of such a project. For domestic refrigeration plans, which cost more because of expensive jigs retrofit, a higher threshold was set. This effectively limited the technology to large companies only and led indirectly to wide-spread use of HCFC-141b in

SMEs. Therefore, if the cost of hydrocarbon technology is not lowered, SMEs can only hope to fall back on environmentally undesirable HFCs, low performing and expensive water-based systems or hope that the Validation/Demonstration of new technologies—will provide more satisfactory options.
The use of hydrocarbon technology has not materially changed over the last 17 years. It requires costly pre-blending equipment, an explosion-free area and special safety procedures. Also, in many countries the systems are unchanged while in Europe significant system optimization has taken place (additives, special polyols, co-blending). UNDP sees options for cost reductions in three areas:

- preblending at supplier level would delete the need for a preblender plus auxiliaries—but cause some increase in the system price;
- direct injection of hydrocarbons would also remove the need for a preblender but increase the equipment cost somewhat;
- the introduction of modern HC blends would allow for lower densities—along with the above-mentioned options and also lower in this way the current operating costs.
- To test the feasibility of these concepts, the development and commercialization of stable pre-blends that can be safely transported and three-component production equipment is required, in addition to the introduction of modern HC blends.

This project is designed in four steps:

4. development, optimization and Validation/Demonstration of premixed, stabilized, modern hydrocarbons systems that can be used directly by foam manufacturers (which means that the blowing agent is incorporated) or used together with direct injection of the blowing agent
5. development of a three component foam dispenser, capable to direct inject hydrocarbons (pentane of cyclopentane blends)
6. placement of the three-component dispenser at a foam manufacturer followed by trials with
    a. direct injection of the blowing agent
    b. using a fully preblended polyol system
4. demonstration of the technology followed by dissemination through an inter-regional workshop

Other PU pilot projects carry a second phase to demonstrate commercial application and include the use of a supplier to develop the necessary systems. There is no need for this in this project. The system part will be an optimization based on knowledge that is already available in Europe and incremental success is virtually assured. Building a three component foaming unit has been before applied in an MLF project through a retrofit so, in this case it will be more of a design optimization than application of a new concept. Also, there is no need to demonstrate the two technology versions in all foam applications. The variations in required formulations are well known to the chemical suppliers that cater HC systems.

Companies do not conduct regular testing on properties of their foams, nor do they set standards. The determination of baseline data on critical properties is a precondition for a successful Validation/Demonstration program. In this case, the supplier of the system will conduct the product testing.

As hydrocarbons are “highly flammable”, UNDP considers the process at the system house (blending) AND at user level (processing) hazardous and requiring adequate safeguards. Current safety requirements are described in UNEP/OzL.Pro/ExCom/25/54 (**Annex 2**). UNDP requires an independent safety audit to be conducted prior to commercial operation of a converted plant (**Annex 3**). Emission monitoring will have to be conducted and, based the outcome modifications/simplifications of the safety requirements can be proposed.

PROJECT IMPLEMENTATION

The project will be implemented through four steps. Following concrete actions are planned:

7. **System Development:** UNDP will contract this out following standard procurement procedures to a qualified chemical supplier (competitive bidding).

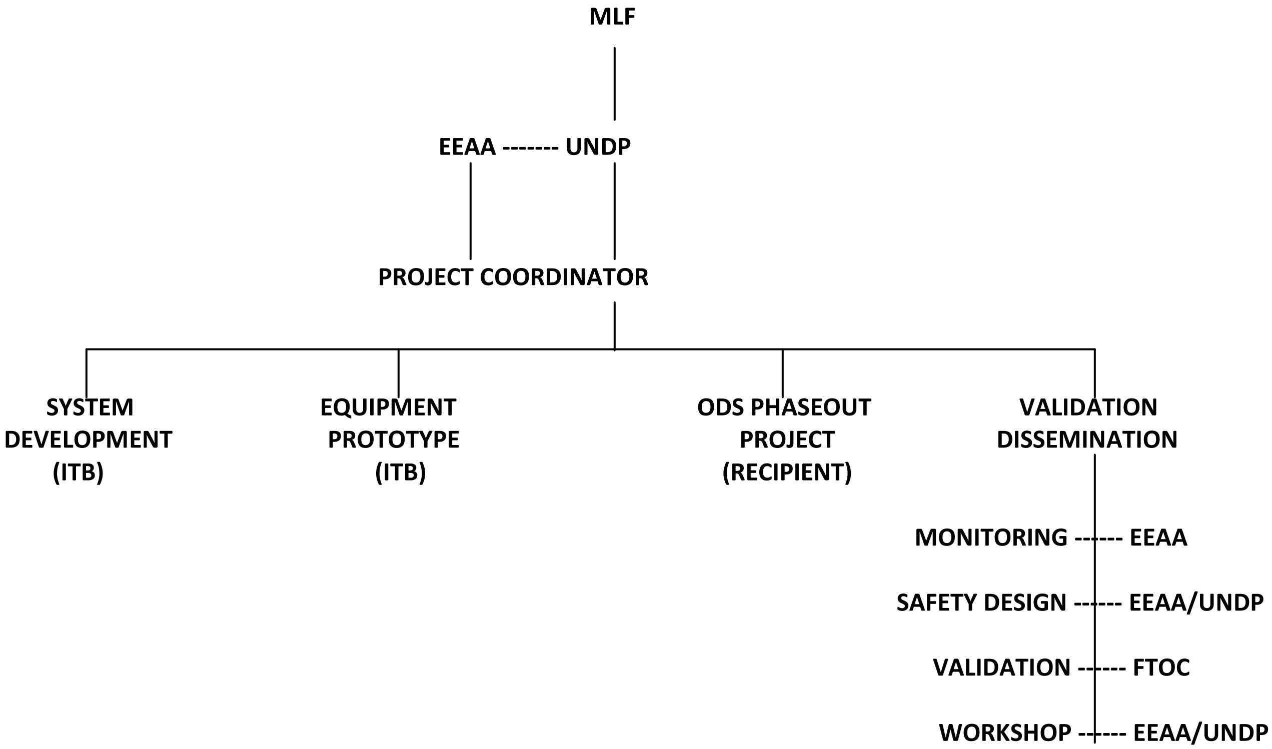
8. **Equipment Development:** as before, UNDP will contract this out to a qualified equipment supplier, following standard procurement procedures.

9. **Trials at a Foam Plant:** A company that is willing to conduct an early phaseout project based on the use of hydrocarbons will be selected as a part of the foam industry survey. The company should have an ODS consumption of around 40 t and have reasonable in-house technical capabilities. 4-5 candidates fit the requirements in Egypt, but here again the Government requested UNDP to select the company through bidding.

10. **Validation:** This will include emission/worker exposure monitoring, design of a safety system and safety procedures, validation of the outcome of the project and holding of an information dissemination inter-regional workshop. These tasks are assigned as follows:

    a. Monitoring - EEAA
    b. Safety design - EEAA/UNDP
    c. Validation - UNEP Foams Technical Options Committee (FTOC)
    d. Workshop - EEAA/UNDP

Following flow chart illustrates the proposed implementation procedure:



4. TECHNICAL OPTIONS FOR HCFC REPLACEMENT IN PU FOAMS

4.1 GENERAL OVERVIEW

Annex-1 provides an overview of all HCFC-141b replacement technologies that are currently available, proposed, or under development. Based on these data, it appears that

- Straight conversion of HCFCs to HFCs will always increase GWP;
- HCs, CO_2 (in its liquid form or derived from water), methylal and methyl formate will be options in PU foams that decrease—virtually eliminate—GWP in PU foams;
- Water-based technologies show serious performance handicaps base on the use of CO_2 as cell gas;
- Technologies such as HBA-2, AFA-L1 and FEA 1100 are not ready for commercialization.

PU validation may therefore be limited to optimized hydrocarbons, methyl formate and methylal.

4.2 HYDROCARBONS AS REPLACEMENT TECHNOLOGY FOR HCFC-141b

HC-based/MLF-supported CFC-phaseout projects have been, along with HCFC-141b, the technology of choice in most refrigeration and in panel applications. The minimum economic size has been typically around 50 ODP t/y or ~US$ 400,000. For domestic refrigeration a handicap was allowed for safety cost, increasing the threshold to ~US$ 600,000. Smaller projects could not pass cost-effectiveness criteria. Consequently, there is no use of HCs in SMEs. In addition, the technology was deemed unsafe for a multiple of applications such as spray and in situ foams. There have been attempts to introduce the use of HCs in those applications—even specially modified equipment was developed for that purpose—but the market has not accepted the use of HCs under what it considers “uncontrolled” conditions. Initially, cyclopentane in different degrees of purity has been used for refrigeration, n-pentane for panels and, not very important in an A5 context, more volatile HCs in one-component foams (OCFs). Fine tuning through HC blends (cyclo/iso pentane or cyclopentane/isobutane) which is now standard in non-A5 countries has not widely spread in A5’s. Investment costs are largely the same as at the time of phasing out CFCs. Consequently, the technology would continue to be too expensive for SMEs and restricted to the same applications as before. However, there are options to fine-tune project costs and investigate other applications:

The introduction of HC blends that will allow lower densities	(lower IOCs)
Direct injection	(lower investment)
Low-pressure/direct injection	(lower investment)
Centralized preblending by system houses	(lower investment)
Application-specific dispensing equipment	(lower investment)

Lowering the conversion costs—either by lowering investment or lowering operating costs—will lower the current eligibility barrier of ~50t/y ODS (based on the current applicable threshold) and widen the pool of potentially eligible users. Important in all these considerations, is that for HC, current incremental operating costs are among the lowest of all replacement technologies. Therefore, from an economic standpoint the use of HCs is one of the most important technologies.

5. PROJECT COSTS

Cost forecasts for pilot projects are problematic as these projects are by nature unpredictable. UNDP has used to the extent possible guidance provided by the Secretariat in Doc 55/47 Annex III, Appendix II. Applying this guidance leads to the following summarized cost expectations:

DEVELOPMENT/OPTIMIZATION/VALIDATION/DISSEMINATION			
#	**ACTIVITY**	**BUDGET (US$)**	**REMARKS**
1	Project Management	10,000	Local expert; see also remark 1
2	Technology transfer, training	30,000	International Expert(s)
3	Testing equipment	55,000	See remark 2 hereunder
4	Production equipment development	125,000	Three-stream high pressure pentane dispenser with standardized, built-in and auxiliary, safety features (modular concept preferred)
5	Preblended systems preparation	100,000	Development: 40,000

			Optimization: 40,000 Validation: 20,000 (at the recipient)
6	Technology Dissemination Workshop	60,000	See remark 3 here-under
7	Peer review/Safety review/Preparation	50,000	Includes - safety audit - design study for centralized HC blending - review by FTOC
8	Contingencies	43,000	10% of sub-total/rounded
TOTAL		**473,000**	

Remark-1: because the design of this project did not allow working through a system house that provides local project management, a local project management expert is required.

Remark 2: Air quality testing and cell gas control will be conducted by EEAA's Air Quality Laboratory and the requested equipment stationed there. It can be used subsequent projects as well and can measure air concentration of all HCFC replacements

Testing equipment	Air quality monitor		35,000 (portable, explosion proof)
	Cell gas analyzer		20,000
	Total	**US$**	**55,000**

Remark 3: After consultations with the MLF Secretariat, it is being proposed to expand the scope of the workshop to an inter-regional workshop of 2-3 days which – while focusing primarily on this project result, would also elaborate on the results of UNDP's other technology-validation projects that were approved (eg methyl formate,, methylal). The workshop would thus discuss various findings of this project, and compare them with the results of those other pilot projects. A site visit at the recipient company will be part of the workshop-agenda. Participants at the workshop will include Egyptian stakeholders who would have interest in the project results, but also relevant MLF experts (national and international) who will be involved in writing future MLF project proposals in the foam sector.

7. IMPLEMENTATION/MONITORING

Following tentative implementation schedule applies:

TASKS	2009				2010			
	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q
Project Start-up								
MF Project Approval			X					
Receipt of Funds			X					
Grant Signature			X					
Monitoring/oversight activities in place			X					
Phase-I								
-Equipment development			X					
-Equipment construction/installation/start-up			X	X				
-System development				X				
-System optimization				X	X			
-System validation at system house				X	XX			
-Peer review/detailed design of phase- II					XX			
-Technology Dissemination Workshop(s)					X			

MILESTONES FOR PROJECT MONITORING

TASK	MONTH*
(a) Project document submitted to beneficiaries	2
(b) Project document signatures	3
(c) Bids prepared and requested	3, 9
(d) Contracts Awarded	3, 9
(e) Equipment Delivered	4, 11
(f) Training Testing and Trial Runs	4, 12
(g) Commissioning (COC)	14
(h) HOP signatures	15
(1) Compliance Monitoring	17

* As measured from project approval

7. ANNEXES

Annex 1:	Overview of HCFC Replacement Technologies in Foams
Annex 2:	Applicable Safety Guidelines (current version)
Annex 3:	Safety Audit (current version)
Annex 4:	Government Transmittal Letter

ATTACHMENT IV:

SAIP
ADVANCED POLYURETHANE EQUIPMENT
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TÜVRheinland
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Organizzazione con Sistema di Gestione certificato
Company with Management System certified
ISO 9001:2008
SINCERT

NEW APPROACHES IN EQUIPMENT FOR HYDROCARBON POLYURETHANE TECHNOLOGY[1]

1. Introduction

Current hydrocarbon (HC) technology is based on in-house preblending of the hydrocarbon with a polyol blend, followed by the actual foam process. UNDP requested SAIP to commission equipment for a pilot project in Egypt that would be able to operate with preblended systems as well as to directly inject pentane into the mixing head (“three component system”) without jeopardizing safety.

This paper addresses the use of

- Currently common HC technology (inhouse preblending);
- Preblended HC systems; and
- Directly injected HCs

It then proceeds with describing the equipment as commissioned and tried in the mentioned pilot project.

2. Currently Common Equipment for HC Technology

The objective of this part of the presentation is to provide an overview of the most common technology for the use of hydrocarbons (HCs) as an alternative blowing agent to HCFCs in polyurethane foam processing for insulation applications.

The use of HCs is a today proven technology which can be:

- Cost effective
- Easy, economical to operate and commercially available
- Easy and convenient processing
- Occupational safe
- Environmental safe

Whatever the applications of HC’s are, the versatility of the available solutions provides a high degree of flexibility and efficiency.

In the discontinuous foaming process a two component foam dispensing machine is used. The Polyol is inhouse preblended with the blowing agent.

The HC is blended with Polyol through the use of dedicated equipment. HC’s and the Polyol are supplied from storage devices and then metered, through a controlled, closed loop system, by dedicated pumps to the premixing station, where they are mixed through a static mixer.

After completion of the mixing process, the Polyol / HCs blend is transferred with a transfer pump to the high pressure foam dispensing machine (s) Polyol tank (s) through a distribution piping or automatically loaded into a buffer tank and then transferred to the highpressure foam dispensing machine(s) polyol tank(s) through distribution piping.

All equipment such as:

- The premixing station
- The buffer tank and the transfer pump
- The foam dispensing machine Polyol

are enclosed in a safety box in order to limit the HCs vapors emissions in a controlled and restricted area. The safety box is provided with safety devices which include double speed fans for forced ventilation complete with suction hoods, extraction chimney, airflow control, detection system (catalytic or infrared sensors) and a safety electric control system (ECS) for management and monitoring of HC vapor emissions.

The safety electric control system (ECS) must be provided with an independent electric power connection in order to guarantee the monitoring and the management of the safeties in case of electric power shut down. The ECS provides the equipment with standard working conditions with one fan in standard operation while starting automatically a second fan with visual and acoustic indication signals if 15% of the LFL (lower explosion level) is reached. The safety electric control system will shut down the electric power and the HCs feeding at 30% of the LEL.

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[1] Presentation to the UNDP workshop on “Innovative Low Cost Hydrocarbon Technologies” in Cairo, Egypt July 4, 2011

All equipment is built according to ATEX 94/9/EC directives European Standard and in conformity with II 2 Gc IIB T4.

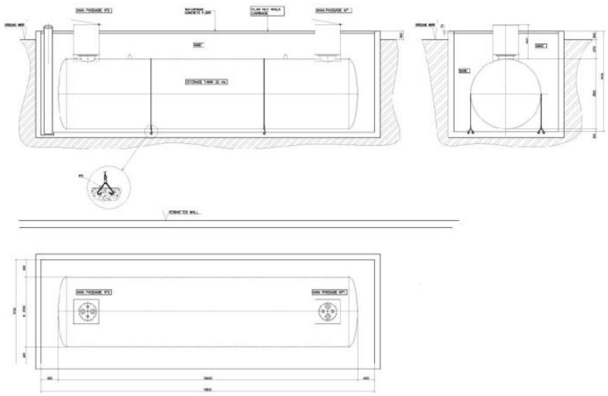
Activities required to introduce HCs in a production facility vary according to geographical area, size of the enterprise, type of production and conditions of the existing facilities.

The use of HCs as blowing agent in polyurethane foam doesn't imply deep changes in the production process but at a minimum the installation of:

- an appropriate HCs storage farm
- a Polyol storage farm (if required)
- the installation of a Polyol / HCs premixing station and related equipment
- the retrofit or the replacement of the foam dispensing machine (s)
- the modifications or the changes, where necessary, of the auxiliaries equipment
- (foaming fixtures, presses, moulds, etc.)
- the installation of the appropriate safety devices for the monitoring and management of the HCs vapours emissions.

The HCs storage farm

HCs are stored in double jacket carbon steel tank (s) , that are placed underground in a reinforced concrete basin or above ground.



The tank(s) are equipped with a proper HC's leakage detection system and are placed in a dedicated area outside the production factory. The tank (s) capacity is in relation to the production consumption. The HCs feeding, from the outdoor storage to the indoor premixing station, is provided by volumetric or pneumatic pumps. The HCs feeding piping to the premixing station is placed partially outdoor and partially indoor and can be assembled underground or above ground. The piping can be manufactured in carbon steel and as a single jacket , as a double jacket with HCs leakage control and with or without external insulation. The single jacketed piping is used above ground in outdoor placement and it is normally externally insulated. The double jacketed piping is used either outdoor and underground in order to prevent HCs leakage with consequent ground contamination, or indoor in order to prevent from fire. Moreover particular precaution in the manufacturing of the double jacketed piping must be taken into consideration in case of areas subject to heart quakes. All the piping must be welded while the flanged or threaded connections should be reduced to the minimum and monitored if indoor.

The size of the pentane storage farm is depending mostly on the production consumption and different typologies of storage farm are available.

The Polyol storage farm

The Polyol is stored either in vertical or IBC tanks in a dedicated storage area. The Polyol metering to the premixing station is provided by a dedicated pump.

The Polyol / HCs premixing station

The Polyol / HCs mixing is performed by a premixing station. The premixing station mainly consist of a static mixer, where Polyol and HC from the storage farms, are metered by special pumps under specific conditions through a closed loop system and mixed by the static mixer. At the end of the mixing process, the Polyol / HCs blend , is automatically transferred with a pump to the high pressure foam dispensing machine (s) Polyol tank (s) through a distribution piping or to a buffer tank.

The foam dispensing machine

The foam dispensing machine is a specially designed equipment suitable for the use of HCs, where the Polyol line is enclosed in a safety box which is provided with all the necessary safety devices.

There are different options related to the foam dispensing machine retrofit or replacement as follows:

- replacement with a complete new equipment
- retrofit of the equipment polyol line where applicable
- retrofit of the polyol line with line replacement

Replacement: The complete new equipment would be composed of:

The isocyanate line in a standard configuration

- No enclosure and ventilation
- No detection system
- No Ex – proof components

The polyol blend line

- Enclosure and ventilation
- Drip pan
- Pipes, hoses, fittings leakage free
- Tank blanketing with nitrogen
- Grounding
- Detection system (sensors)
- ATEX components (e.g. tank levels, tank heating elements, etc.)
- Magnetic coupling for the dosing pump with motor
- Magnetic coupling for the tank stirrer with motor

The polyol line meets European standard ATEX 94/9/EC and is in conformity to II 2 Gc IIB T4.

The mixing head

High pressure self cleaning linear or laminar flow at two components and provided with nitrogen flushing prior the pouring into a closed cavity. All electric components assembled on the mixing head are ATEX standard.

The retrofit of the equipment polyol line where applicable

It consist on the replacement of all the components of the line to be in compliance with the ATEX safety standard. This method is applicable to those equipment where conditions are applicable and not high costs are involved.

The retrofit of the polyol line with line replacement

It consist on the replacement of the whole Polyol line. This method is applicable to those equipment where conditions are not applicable for the retrofit of the components of the Polyol line to be in compliance with the ATEX safety standard.

The auxiliaries equipment

Very important is the retrofit of the auxiliaries equipment such as foaming fixtures, moulds, foaming presses, etc. to avoid the pentane concentration and the ignition source.

The retrofit consist in the application of:

- A proper ventilation and exhaust system
- A proper detection system (sensors)
- The grounding of the equipment
- The use of ATEX components

The zones classification

An important aspect for the conversion of a production facility to the use of HC and the retrofit of the auxiliaries equipment, is the zones classification.

Zones are classified according to the European Directive CEI EN 6007910 in : Zone 0, 1 and 2.

The zone classification is defined in respect of different factors such as pentane vapours emission and their accumulation in the area and the ambient ventilation in the area. That is why, detection and forced artificial and localized ventilation is required as well as other safety measures to avoid ignition sources.

3. Preblended HC Systems

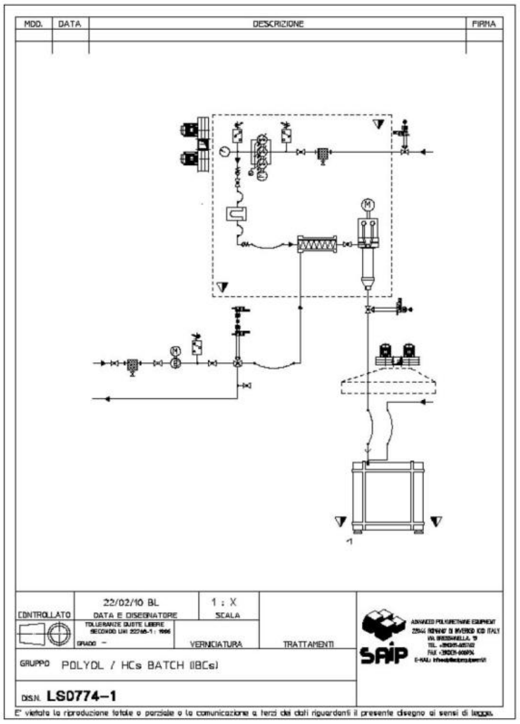
Fully formulated HCbased polyols can be supplied in drums or IBC tanks as readytouse PU systems.

The advantage of using Polyol / HC blends supplied through IBCs is that there is no need to install an HC storage farm and a Polyol / HC premixing station.

The foaming equipment retrofit or replacement concept remains unchanged and as follows :

- replacement with a complete new equipment
- retrofit of the equipment polyol line where applicable
- retrofit of the polyol line with line replacement

Concerning retrofit of auxiliary equipment such as foaming fixtures, moulds, foaming presses, etc., as previously mentioned, the same concept applies to avoid pentane concentrations and the ignition sources. Zoning remains according to the European Directive CEI EN 6007910 in : Zone 0, 1 and 2. The zone classification is defined in respect of different factors such as pentane vapours emission and their shell life in the area and the ambient ventilation in the area. That is why, detection and forced artificial and localized ventilation is required as well as other safety measures to avoid ignition sources.



4. Directly injected HCs

HC’s can also be injected as third stream directly into the mixing head.

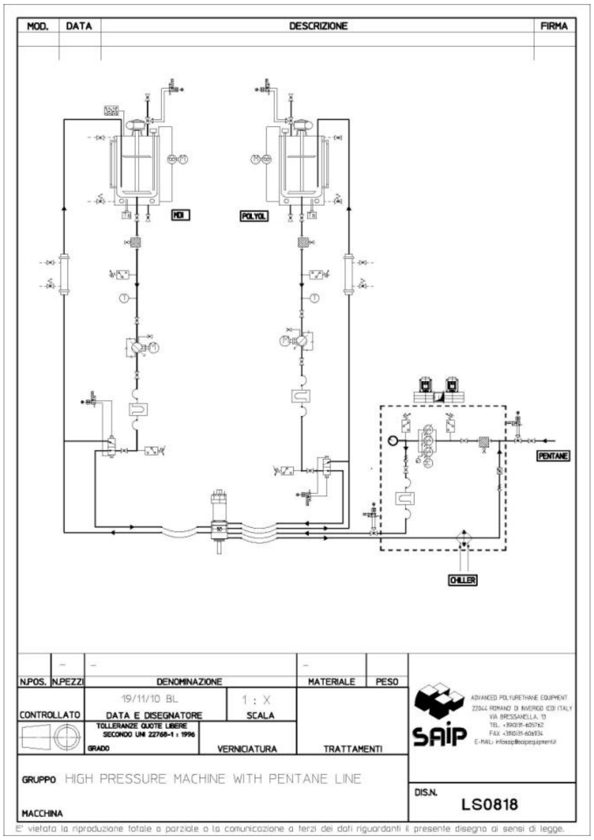
For the third stream injection the following equipment is needed:

- an appropriate HC’s storage farm
- a HC’s high pressure dosing unit complete with cabin and ventilation
- a high pressure mixing head with third stream
- the modifications or the changes, where necessary, of the auxiliaries equipment (foaming fixtures, presses, moulds, etc.)
- the installation of the appropriate safety devices for the monitoring and management of the HCs vapours emissions.

This technology presents a series of advantages:

- With third stream injection the existing 2 component dosing equipment can be used
- There is no need for a premixing station
- No losses of HC’s during premixing, shelf life etc.
- No issues with contamination in case different polyols will be used
- Third stream injection allows to change the HC percentage at every shot

Concerning retrofit of auxiliary equipment such as foaming fixtures, moulds, foaming presses, etc., as previously mentioned, the same concept applies to avoid pentane concentrations and the ignition sources. Zoning remains according to the European Directive CEI EN 6007910 in : Zone 0, 1 and 2. The zone classification is defined in respect of different factors such as pentane vapours emission and their shell life in the area and the ambient ventilation in the area. That is why, detection and forced artificial and localized ventilation is required as well as other safety measures to avoid ignition sources.



5. The Egypt pilot project – Equipment development

The UNDP project intends to optimize, validate and disseminate the use of low cost hydrocarbon technology in the manufacture of PU rigid insulation for small and medium sizes enterprises. For this purpose UNDP requested foam dispensing equipment that is able to use a premixed Polyol / HC blend along with the option to metering HC as a third stream directly into a mixing and pouring head.

The resulting equipment is a three components dispensing unit and composed as follows :

The isocyanate line in a standard configuration

- No enclosure and ventilation
- No detection system
- No Ex – proof components

The polyol / HC blend line

- Enclosure and ventilation
- Drip pan
- Pipes, hoses, fittings leakage free
- Tank blanketing with nitrogen
- Grounding
- Detection system (sensors)
- EX–proof components (tank levels, tank heating elements, etc.)
- Magnetic coupling for the dosing pump with motor
- Magnetic coupling for the tank stirrer with motor
- Closed loop mixing device (static mixer)

The polyol line meets European standard ATEX 94/9/EC and is in conformity to II 2 Gc IIB T4.

The HC line

- Enclosure and ventilation
- Drip pan
- Pipes, hoses, fittings leakage free
- Tank blanketing with nitrogen
- Grounding
- Detection system (sensors)
- EX – proof components
- Magnetic coupling for the dosing pump with motor
- Magnetic coupling for the tank stirrer with motor

The HC line meets European standard ATEX 94/9/EC and is in conformity to II 2 Gc IIB T4.

The mixing head

High pressure self cleaning laminar flow at three components and provided with nitrogen flushing device. All the electric components assembled on the mixing head are ATEX standard.

6. Conclusions

The aim of the project, as mentioned before, is to compare the foam characteristics of of two different HC foaming methods—a preblended and a third stream system—against a baseline HCFC141b based system. From an equipment perspective, this objective has been achieved.

Based on the experience gained from this project we can say today that it is possible to

- retrofit existing equipment to the use of HC as a third stream, where applicable, with a cost saving investment and with proper results and performances;
- to avoid an HC premixer with auxiliaries by using properly stabilized preblended systems with a cost saving investment and with proper results and performances

The project finalization was possible thanks to

- SAIP's previous experience in this type of equipment and technology;
- To the joint cooperation with Dow Chemical which was supporting the project with chemical tests and trials in their Cairo laboratory; and
- To the support of the UNDP organization.

Dow Chemical will give you a more detailed comparison and result by the chemical point of view.

7. Further Developments Anticipated

Even if the results of the tests have proven the efficiency and repeatability of the mixing with third stream injection SAIP is already working on further improvement of the mixing based on the mixing results for limit applications.

THANKS FOR YOUR ATTENTION

ATTACHMENT V

UNDP Egypt project workshop, Cairo 2011

The Dow Chemical Company

Report of data generated in DOW Cairo Polyurethane System House laboratory with DOW systems and SAIP novel high pressure dispensing machine for discontinuous production processes, convertible from traditional pre-blended pentane injection to third stream pentane addition directly in the mix head.

Sustainability is a key challenge for many industries around the world. DOW Formulated Systems, as the polyurethane industry is strongly committed to this theme by continuously developing formulations and solutions that help preserving the environment. In particular Rigid Foams, with their insulation performance, significantly contribute to meet energy-saving requirements.

The development of sustainable polyurethanes formulations includes the transition from blowing agents (BAs) showing an Ozone Depletion Potential (ODP) to Zero ODP technologies. The selection of the right alternative blowing agent technology and machine to dispense it should be guided by the critical foam performance and production process requirement, that differ application by application and even producer by producer.

In general DOW Formulated Systems works on a broad spectrum of solutions and blowing agents, and has a broad portfolio of Rigid Foam systems for all the different applications in consideration of the fact that each customer type has its own needs and need tailored solutions.

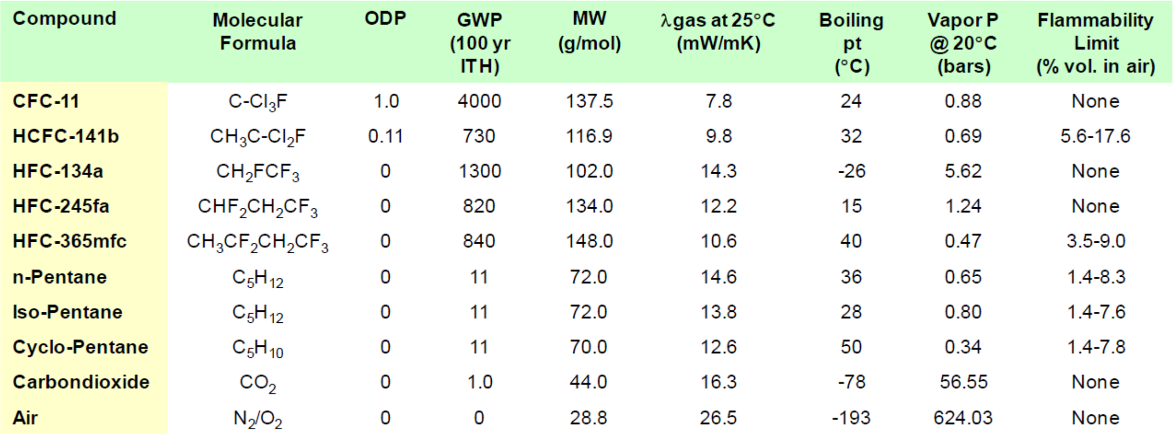
On top of collaborating directly with its customers, Dow is also active in collaborate in external initiatives related to sustainable and effective technologies, aiming at their dissemination, or to test new options that could make them more affordable to the industry. For this reason DOW has made its products and laboratory available for the specific of this UNDP project, to host SAIP equipment and generate data.

Among proven Zero ODP blowing agent options, which include hydrocarbons, hydro-fluorocarbons and water, hydrocarbons are the most utilized, thanks to the good mix of performance features (final foam properties, processing window, cycle time) and low cost, in particular in the domestic appliance industry and continuous laminated sandwich panels industry, but not only. Still, part of the smaller producers in applications like for example commercial appliances, water heaters and discontinuous panels, face the limitation of the investment required to handle the flammability aspects.

Worth to remind that other technologies are available that do not require particular investment, like water blown, that despite it cannot compete with hydrocarbons in terms of applied density and thermal conductivity, represents a good bridge technology for some of the producers, and also high water / low HFC level technologies, which mitigate the HFCs GWP impact, and can help producers to bridge time till new Zero ODP and low GWP blowing agents like HFOs will be available.

Product design with pentane for discontinuous applications along the years addressed various potential initial issues like higher flammability of foams blown with pentane, that needed to be properly addressed by polymer modification, and the different properties of the various pentane isomers, which differ in polyol solubility, thermal insulation performance and boiling temperature, with impact on processing and final foam properties. Typical discontinuous foam production process involves the addition of pentane to the polyol component via a premix unit before metering and the recycling of the blend through the mixing head, therefore a homogeneous blend of the polyol with pentane is needed.

Table 1 below reports properties of the different pentane isomers, in a comparative with HCFC141b and other Zero ODP molecules.



Compound	Molecular Formula	ODP	GWP (100 yr ITH)	MW (g/mol)	λgas at 25°C (mW/mK)	Boiling pt (°C)	Vapor P @ 20°C (bars)	Flammability Limit (% vol. in air)
CFC-11	$C\text{-}Cl_3F$	1.0	4000	137.5	7.8	24	0.88	None
HCFC-141b	$CH_3C\text{-}Cl_2F$	0.11	730	116.9	9.8	32	0.69	5.6-17.6
HFC-134a	CH_2FCF_3	0	1300	102.0	14.3	-26	5.62	None
HFC-245fa	$CHF_2CH_2CF_3$	0	820	134.0	12.2	15	1.24	None
HFC-365mfc	$CH_3CF_2CH_2CF_3$	0	840	148.0	10.6	40	0.47	3.5-9.0
n-Pentane	C_5H_{12}	0	11	72.0	14.6	36	0.65	1.4-8.3
Iso-Pentane	C_5H_{12}	0	11	72.0	13.8	28	0.80	1.4-7.6
Cyclo-Pentane	C_5H_{10}	0	11	70.0	12.6	50	0.34	1.4-7.8
Carbondioxide	CO_2	0	1.0	44.0	16.3	-78	56.55	None
Air	N_2/O_2	0	0	28.8	26.5	-193	624.03	None

C-pentane is more soluble than n-pentane or i-pentane. Solubility, which is also formulation dependant of course, with c-pentane can approach typically 13-15 pbw, while with n-pentane hardly reach 9-10 pbw. Direct comparison of c-pentane with n-pentane typically results in better processing and cycle time for n-pentane (better flow and faster demold) and different combination of final foam properties depending on pentane isomer used (better compressive strength and better dimensional stability for n-pentane - as indicated by the results of the creep test - while a better thermal conductivity occurs with c-pentane).

C-pentane is the preferred choice for those applications where the thermal conductivity is a key property; n-pentane offers better economics thanks to the stronger mechanical properties/better dimensional stability.

OBJECTIVE OF THE PROJECT

Project workshop with SAIP new dispensing unit in DOW Cairo laboratory targeted to validate:

- The suitability of new third stream pentane addition in high pressure dispensing unit for discontinuous production process, to achieve similar foam performance compared to that obtained by processing of pre-blended hydrocarbon polyurethane systems.

- The performance achievable with Hydrocarbon blown polyurethane systems, in comparison with HFCF 141b technologies in use in the Egyptian market, providing a useful guide for the polyurethane foam manufacturers and end-users.

- The impact of addition of hydrocarbons on physical and chemical shelf life of polyols when considering a scenario of pre-blending done by the system supplier (longer shelf lives requested), and not by the foam producer (the latter being the current standard scenario in the industry)

For reasons explained above in the introduction, the experimental program for data generation encompassed different applications, from commercial appliance systems to discontinuous panels systems and water heater systems, and different pentane isomers, the typical ones in use for each type of applications, plus one comparative between two different pentane isomers as example of what is widely reported already in the literature in terms of the different pentane isomers performance.
For each system, data with hydrocarbon technology were generated both in pre-blended pentane way and in third stream pentane addition way, and finally in comparison with transitional HCFC 141b technology.

Six different systems have been selected covering three different applications, as reported in Table 2:

Application ->	Commercial Refrigeration	Discontinuous Panels	Water Heaters
Blowing agent			
HCFC141b	System A	System C	System E
c-pentane	System B	System D	System F
n-pentane		System D	

Systems were tested according to Dow’s internal testing protocol that provides the following:

- Foam reactivity profile and process-ability
- Mechanical, dimensional and thermal properties

In addition, physical and chemical stability of fully formulated polyol blend were tested.

EXPERIMENTAL

Laboratory set up to handle pentane

An Environmental, Health and Safety Risk Assessment was performed before and after installing SAIP HP machine in DOW Cairo laboratory.

In addition to standard EH&S practices in place already to handle HCFC141b systems trials, DOW Cairo laboratories were equipped to handle safely the new HP pentane machine from SAIP (which already included all the sensors system), essentially by upgrading the ventilation system and defining proper position and installing external pentane drums storage, directly connected to HP machine through a pneumatic pump system, as shown in Picture 1.

Picture 1: External pentane storage

Analytical

For all experiments reported in this project determination of blowing agent level in polyol blend was done using standard Quality Control analytical techniques respectively for water (ASTM E203 , Karl Fischer equipment) and for physical blowing agent (DOW internal method, gas chromatographic determination).

Picture 2: Quality Control laboratory

Physical stability and chemical stability of the polyol blend

The evaluation of the blowing agents' physical stability in fully formulated polyols was performed by studying the total blend stability at room temperature along time. After properly mixing the fully formulated polyol with the blowing agent, 200 grams (0.44 lb) of the blend were poured into a glass bottle (capacity: 0.09 gal, 350 ml), visually monitoring phase separation at regular intervals. The formation of an "emulsified" phase or "clear" phase was also noted. Analytical determination of pentane level was also performed.

The chemical stability of the polyol blends was evaluated by storing the fully formulated blends at room temperature and at 50°C, and by performing reactivity and free rise density measurements after specific time intervals.

Foam Properties Evaluation

The high pressure dispensing unit process conditions were as follows: mixing pressure of 150 bar, polyol and isocyanate temperature of 20 – 22°C and output of 250 g/s. Samples taken from Brett mold 200x20x5cm were used to measure the thermal conductivity, average density distribution (ADD), minimum filling density (MFD), and compressive strength (CS). Demold expansion measurements were taken from panels produced in Jumbo 40x70x10 cm molds. The data listed in this report are from 5%, 10% and 15% over-packed foams. Reactivity and free rise density measurements were taken from samples foamed in a bag.

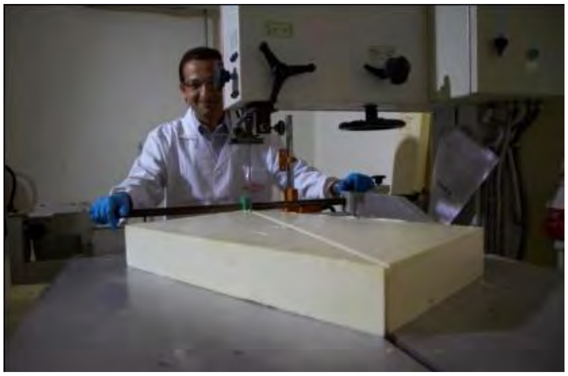
Picture 3,4: Injection free rise density box

Picture 5,6: Extraction from brett mold, injection in jumbo mold and extraction of produced foam

Mechanical properties: compressive strength

Compressive strength was measured according to EN 826 standard. The test was performed on the 10 x 10 x 5 cm specimens, cut from Brett panels, in the direction perpendicular to the growth of the foam (direction of the foam thickness). It was determined as the average value of 5 specimens taken in different positions covering the whole brett panel length.

Picture 7: Band saw cut of specimens for physic-mechanical properties testing



Picture 8,9: compressive and tensile strength testing with dynamometer

Dimensional Stability

The test was performed according to (EN 1604) UNI 7891. The test specimens, 8x8x4 cm in size were conditioned both at high (+80°C) and low temperature (-25°C) for 20 h.

Tensile bond strength (Adhesion test)

The test was performed according to EN 14509 (European product standard for sandwich panels) which refers to EN 1607.

The foam adhesion to the two facings (top and bottom) was measured simultaneously through a tensile test, perpendicular to the facings.

Thermal conductivity

Thermal conductivity was measured according to EN 12667 and/or ASTM C 518. The test was performed on specimens 20 x 20 x 2.5 cm.

Picture 10,11: Thermal conductivity specimens and testing equipment

RESULTS AND DISCUSSION

Design of experiment on systems for Commercial Appliance

In a first set of experiments, formulated systems for appliance applications have been tested running a Design of Experiment in order to gather a clear understanding of similarities /difference when running a pre-blended hydrocarbon approach versus a third stream one, by running different pentane levels and different injection times. Finally a comparison with a reference commercial HCFC141b system, System A, was performed.

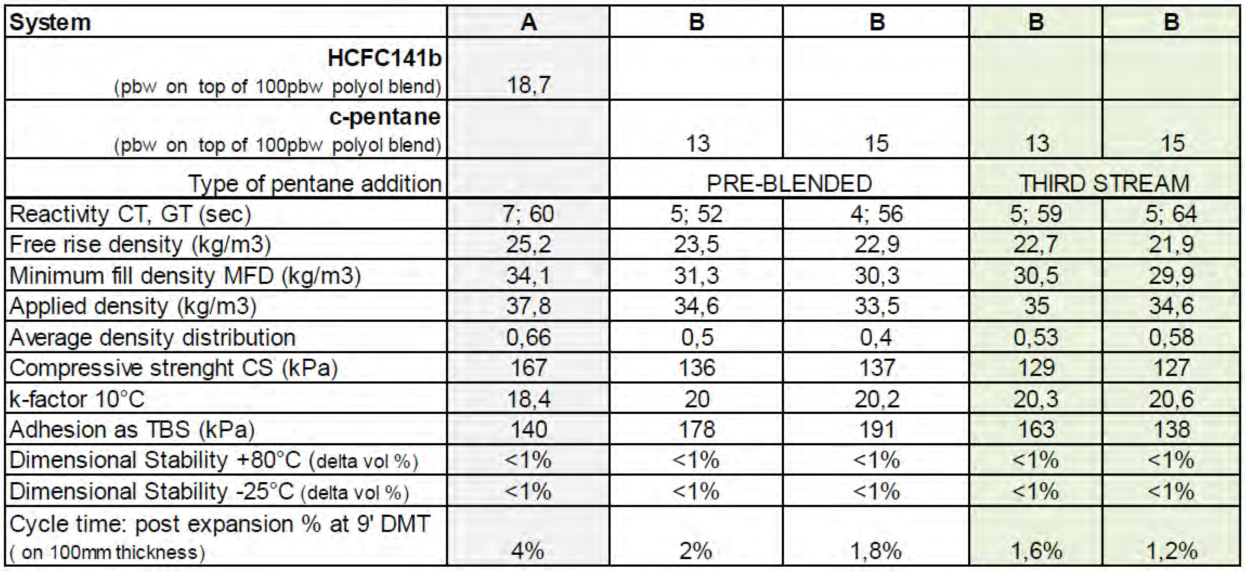
As reported in the introduction, there are 3 isomers of pentane, and among them c-pentane is the preferred choice for those applications where the thermal conductivity is a key property.

A design of experiment was run on System B (c-pentane blown), and two variables were selected in order to run full comparison:

- Pentane addition (2 types of pentane addition, categorical)
- BA level (2 levels, continuous variable)

In addition, some repetition was performed in order to determine data reproducibility, resulting in a complete series of more than 12 full machine evaluations and testing.

Also, considering that in third stream addition, the polyol blend enters the mixhead still without pentane and therefore with much higher viscosity vs a polyol already containing pentane, and the contact time before injection is extremely short, one additional run was performed heating the polyol bled up to 30°C in order to check if lower viscosity has an impact on the yield of the third stream. Results showed that lower polyol viscosity in this case does not impact results. In the specific of third stream, before running full evaluation, the reproducibility of injection and the consistency of the foam resulting out of it, from the start to the end of injection, was checked by specifically pouring long sections in free rise density and checking structure and resulting density and density distribution homogeneity. This exercise confirmed consistent yield and results during injection.



System	A	B	B	B	B
HCFC141b (pbw on top of 100pbw polyol blend)	18,7				
c-pentane (pbw on top of 100pbw polyol blend)		13	15	13	15
Type of pentane addition		PRE-BLENDED		THIRD STREAM	
Reactivity CT, GT (sec)	7; 60	5; 52	4; 56	5; 59	5; 64
Free rise density (kg/m3)	25,2	23,5	22,9	22,7	21,9
Minimum fill density MFD (kg/m3)	34,1	31,3	30,3	30,5	29,9
Applied density (kg/m3)	37,8	34,6	33,5	35	34,6
Average density distribution	0,66	0,5	0,4	0,53	0,58
Compressive strenght CS (kPa)	167	136	137	129	127
k-factor 10°C	18,4	20	20,2	20,3	20,6
Adhesion as TBS (kPa)	140	178	191	163	138
Dimensional Stability +80°C (delta vol %)	<1%	<1%	<1%	<1%	<1%
Dimensional Stability -25°C (delta vol %)	<1%	<1%	<1%	<1%	<1%
Cycle time: post expansion % at 9' DMT (on 100mm thickness)	4%	2%	1,8%	1,6%	1,2%

Table 3: Commercial Appliance Systems, average results from laboratory HP machine trials; selected extraction out of overall performance elements tested.

Overall data set from the Design of Experiment has been analyzed using a statistical tool.

Effect of type of addition: third stream vs pre-blended

In Table 1 it can be seen addition of pentane third stream has a slight influence in terms of slowing down the gel time reactivity of selected system, but it is not expected per se to be critical. Third stream addition of pentane , in the specific of System B has a positive effect in lowering the free rise density in this case (better blowing efficiency), while flow of the system remains similar to pre-blended. In principle this seem to indicate that third stream could allow to go for slightly lower applied densities, but in the case of System B we decided to report properties at same applied density of pre-blended system , as it is not designed to go for lower applied densities, which could remain an area of further study.

Chart 1 exemplifies part of statistical analysis, and visualizes result of free rise density means comparison for System B at 13 pbw pentane, third stream vs pre-blended, and the two distinct rings on the right are just confirming that difference is significant.

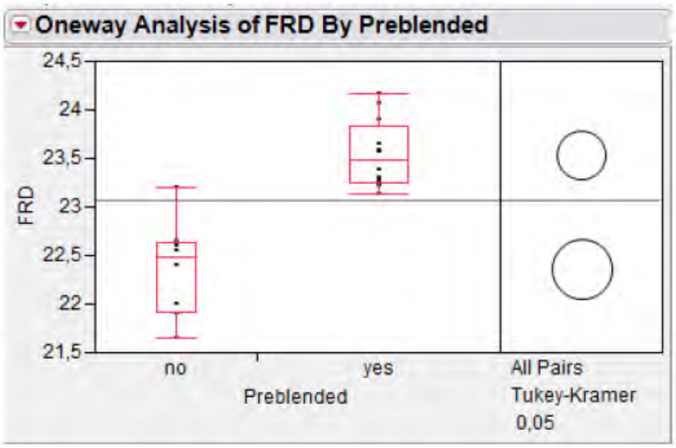


Chart 1: Free rise density comparative analysis third stream (left) vs preblended (right)

Required process temperatures and resulting mechanical properties, dimensional stability, and process conditions are confirmed to be similar between the two pentane addition methods, only adhesion shows some lower values in the case of third stream vs pre-blended, but still in an overall range of acceptable values based on industrial experience.

Thermal conductivity is slightly worse in the case of third stream addition of pentane. The reason for this behavior is still under investigation, pending results of cell structure analysis and cell size determination of the produced foams. First hypothesis is that this is the result of slower reactivity that we get with third stream, as the separate entrance of pentane directly in mix head absorbs mixing energy cooling down the reaction mixture. An optimization of the pentane injection pressure might eliminate this difference, according to machine supplier.

In third stream addition, the polyol blend enters the mixhead still without pentane and therefore with much higher viscosity vs pre-blended polyol already containing pentane; in addition,the contact time between pentane and the other liquid components, isocyanate and polyol, before injection is extremely short. For this reason it was decided to do one additional run heating the polyol bled up to 30°C in order to check if lower polyol viscosity has an impact on the yield of the third stream. Results showed that lower viscosity in the specific of System B did not impact results.

Comparison with current HCFC141b technology in the market

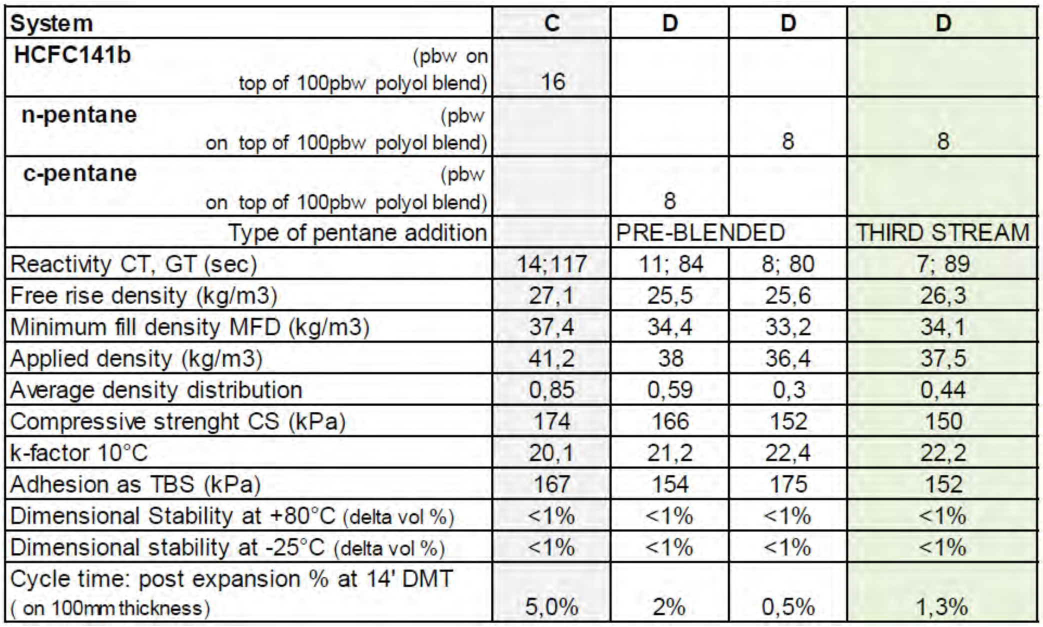
As known in the literature and from years of industrial experience, also in the specific of this workshop the comparison between hydrocarbon blown System B with HCFC141b blown System A in use in Egyptian market for commercial refrigeration show that pentane based solutions are in general characterized by lower applied densities compared to HCFC 141b blown systems. One of the reasons is that the flow ability is better in the case of HC pre-blended solutions , as indicated by flow index (flow index = MFD/FRD) and by average density distribution values. Another reason is that, as known in the literature, HCFC141b has some plasticizing effect on the polyurethane foam, which needs to be offset by applying high enough density on top of proper formulation.

Foam compressive strength is lower in the case of pentane blown, due to the lower applied density, but in acceptable range of values for this technology. In terms of processing temperatures pentane technology of System B has wider processing window than System A with HCFC141b, which is more sensitive to cold mold temperatures. Finally a clear worsening of foam insulating properties is observed with c-pentane based technology vs HCFC141b.

Systems for Discontinuous Panels application

For cold storage discontinuous panels (DCP) application a direct comparison between System D (HC based system) and System C (HCFC 141b based system) was performed. Two different pentane isomers, cyclo-pentane and normal-pentane, were included in the evaluation for System D. Only one level of pentane was considered.

Table 4 reports main properties summary results from comparison of HC blown technology performance, both pre-blended and third stream addition option, vs HCFC 141b blown technology.



System	C	D	D	D
HCFC141b (pbw on top of 100pbw polyol blend)	16			
n-pentane (pbw on top of 100pbw polyol blend)			8	8
c-pentane (pbw on top of 100pbw polyol blend)		8		
Type of pentane addition		PRE-BLENDED		THIRD STREAM
Reactivity CT, GT (sec)	14;117	11; 84	8; 80	7; 89
Free rise density (kg/m3)	27,1	25,5	25,6	26,3
Minimum fill density MFD (kg/m3)	37,4	34,4	33,2	34,1
Applied density (kg/m3)	41,2	38	36,4	37,5
Average density distribution	0,85	0,59	0,3	0,44
Compressive strenght CS (kPa)	174	166	152	150
k-factor 10°C	20,1	21,2	22,4	22,2
Adhesion as TBS (kPa)	167	154	175	152
Dimensional Stability at +80°C (delta vol %)	<1%	<1%	<1%	<1%
Dimensional stability at -25°C (delta vol %)	<1%	<1%	<1%	<1%
Cycle time: post expansion % at 14' DMT (on 100mm thickness)	5,0%	2%	0,5%	1,3%

Table 4: Extraction of data resulting from polyurethane foams for discontinuous panel applications produced with HP machine.

Effect of type of addition: third stream vs pre-blended

For System C the general performance of third stream and pre-blended technology can be considered aligned between third stream and pre-blended pentane addition. All differences observed were in fact within the variability ranges of measurement methods used in the evaluation.

N-pentane vs c-pentane comparison

This experiment exemplifies what reported in the literature and in this report introduction about the different performance of these two pentane isomers, confirming that n-pentane in general gives:

- improved flow properties which can lead to lower applied density

- improved mechanical properties and dimensional stability

- improved cycle time properties
- worse k-factor

Comparative with current HCFC141b technology in the market

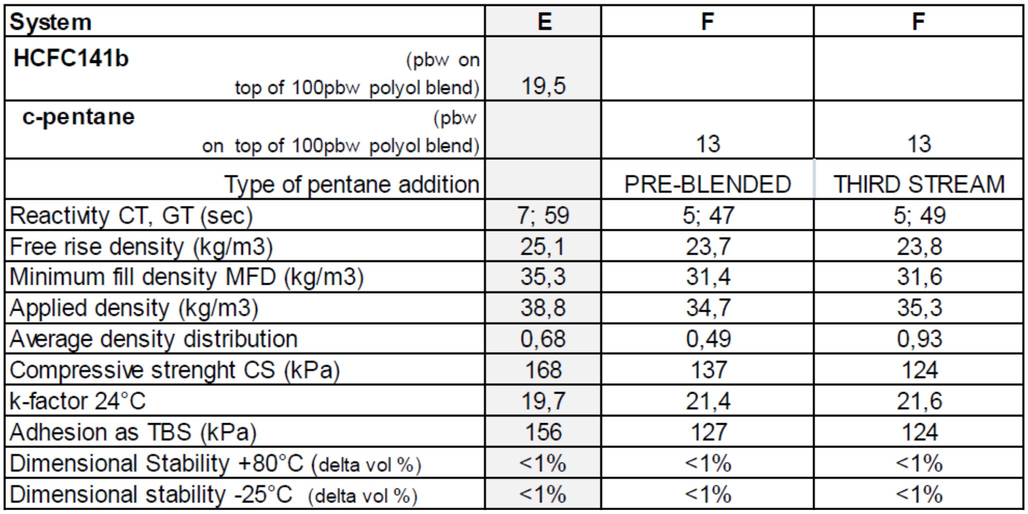
Pentane based System D allows lower applied density compared to HCFC141b blown System C while keeping good foam properties (compressive strength, dimensional stability and adhesion to metal facings). Flow ability is slightly improved. Cycle time and process temperature latitude are improved when using pentane.

Only drawback observed with pentane based technology is the foam thermal conductivity: a 5-6% worsening was in fact observed with c-pentane and it was extended to 11% when using n-pentane.

Systems for Water Heater application

For water heaters a direct comparison of System E (HCFC141b blown) and F (HC blown)was performed. Only one level of pentane was run.

Table 5 reports main properties summary results from comparison of HC blown technology performance, both pre-blended and third stream addition option, vs HCFC 141b blown technology.



System	E	F	F
HCFC141b (pbw on top of 100pbw polyol blend)	19,5		
c-pentane (pbw on top of 100pbw polyol blend)		13	13
Type of pentane addition		PRE-BLENDED	THIRD STREAM
Reactivity CT, GT (sec)	7; 59	5; 47	5; 49
Free rise density (kg/m3)	25,1	23,7	23,8
Minimum fill density MFD (kg/m3)	35,3	31,4	31,6
Applied density (kg/m3)	38,8	34,7	35,3
Average density distribution	0,68	0,49	0,93
Compressive strenght CS (kPa)	168	137	124
k-factor 24°C	19,7	21,4	21,6
Adhesion as TBS (kPa)	156	127	124
Dimensional Stability +80°C (delta vol %)	<1%	<1%	<1%
Dimensional stability -25°C (delta vol %)	<1%	<1%	<1%

Table 5: Extraction of data resulting from polyurethane foams for water heater applications produced with HP machine

Effect of type of addition: third stream vs pre-blended

All properties resulted statistically equivalent with both pentane addition approaches. All differences observed were in fact within the variability ranges of measurement methods used in the evaluation.

Comparative with current HCFC141b technology in the market

Pentane blown System F is characterized by lower applied density compared to HCFC141b commercial System E. The flow ability is slightly improved. Compressive strength values and adhesion values are lower for the pentane system, mainly due to 10% lower applied density reduction, but still within the acceptable range for the technology and application. Cycle time and required process temperature conditions are aligned.

Again a 9% worsening of foam insulating properties is observed with pentane based technology vs HCFC141b blown system.

Shelf life study on pentane pre-blended systems.

Most standard practice today in the industry is to have polyol blend supplied without pentane to the foam manufacturers by system supplier, and then foam manufacturers directly pre-blendes at his site the pentane to the polyol blend through a premix unit. This type of operation typically does not require pentane to be stable in polyol blend for long time, and shelf life of polyol blends without pentane is not critical.

A different situation would be represented by a practice where the system supplier already pre-blends pentane in its polyol blend, and supplies it fully formulated to the foam manufacturer. In this case pentane would need to be stable in the polyol blend for some months, typically 6 months, which in principle is a quite critical situation especially for the less soluble pentane isomers like n-pentane, and extremely critical situation in case the suggested storage temperature conditions both during handling, shipping and storage are not fully respected. Of course the shelf life behavior would be formulation dependant as well.

Worth to mention that is this second scenario, the topic of investing to handle flammability aspects and risks of pentane would be extended to a larger number of players, as supplier would have to invest to handle pentane in its operation, and as polyol blends containing pentane have flash point and are flammable materials, with additional costs upstream in the value chain to be sustained by suppliers, and that would reflect into system price.

Nevertheless, in order to understand the criticality of such scenario, shelf life of pre-blended polyol with pentane was studied for a prolonged time period to understand criticality.

System B (c-pentane blown) for commercial appliance was tested, and also System D (n-pentane blown) for cold room discontinuous panels was tested.

The evaluation of pentane physical stability in fully formulated polyol stored in 1 liter bottles was performed by studying the blend stability at two temperatures, room temperature and 50°C, during time, preparing pre-blends as discussed in the experimental section. Visual inspection was run at regular intervals. The formation of an “emulsified” phase or “clear” phase was also noted.

The evaluation of fully formulated blends chemical stability was performed only in case physical stability was still ok, and it was done by performing reactivity and free rise density measurements after specific intervals.

For this study the same systems utilized in the rest of the project were studied, and not reformulation work has been done, in particular System B (c-pentane blown) and System D (n-pentane blown).

Aging of blends is still ongoing, at this stage we have reached 3.5 months for the c-pentane system tested, and we have stopped the aging of the n-pentane system for reasons reported below.

<u>c-pentane preblended polyols physical and chemical stability</u>

3 months aging of fully formulated polyol of system B containing c-pentane gave good physical stability at room temperature, with no c-pentane separation observed, as reported in Table 6 below. On the other side it is clear from analytical that sample with higher initial level of pentane lost more pentane during aging (data are not representative exactly of what would happen in bigger containers like drums or IBCs, but should be taken as indications). Temperature of 50°C is more critical and resulted in a color change of the blend.

Chemical stability is almost ok at room temperature, with some acceleration of reactivity partially due to loss of pentane, while at high temperature more variation is appreciated along time, with high loss of pentane from liquid phase (despite bottles sealing) during storage and operations.

System B	**pentane content**		**physical stability**	**chemical stability**	
(c-pentane)	analytical ctrl			reactivity GT	free rise density
	%		visual	(sec)	(kg/m3)
	sample 1	sample 2	sample 1,2	sample 1,2	sample 1,2
Room T 23°C					
initial	13	14,5	ok	ok	ok
after 1 month	-	-	ok	slightly faster	ok
after 2 months	-	-	ok	faster	ok
after 3 months	12,4	12,8	ok	faster	ok
High T 50°C					
initial	13	14,5	ok	ok	ok
after 1 month			ok	slightly faster	similar
after 2 months			ok	faster	slightly higher
after 3 months	6,9	6,6	change of colour	faster	slightly higher

Table 6: shelf life behavior of System B studied at two different temperatures.

As a graphic example out of full data set, the free rise density variation at 50°C storage temperature is reported below.

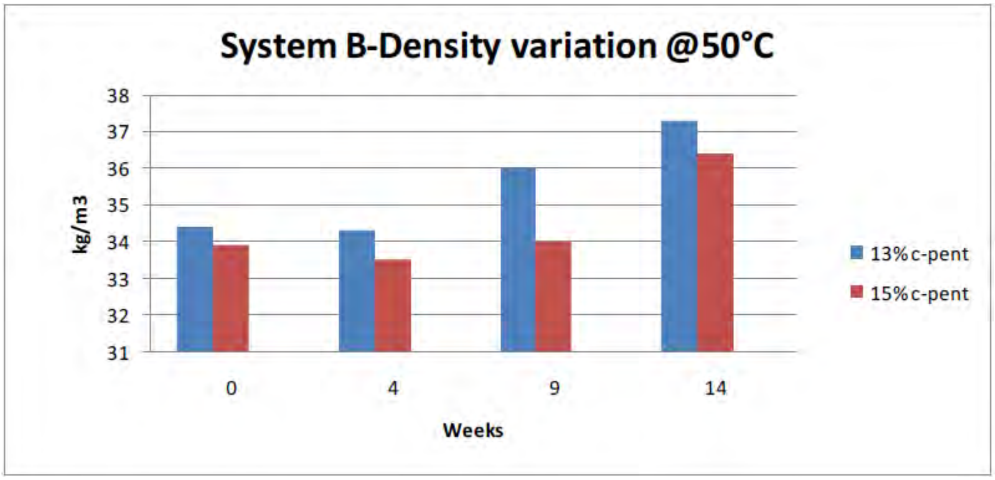
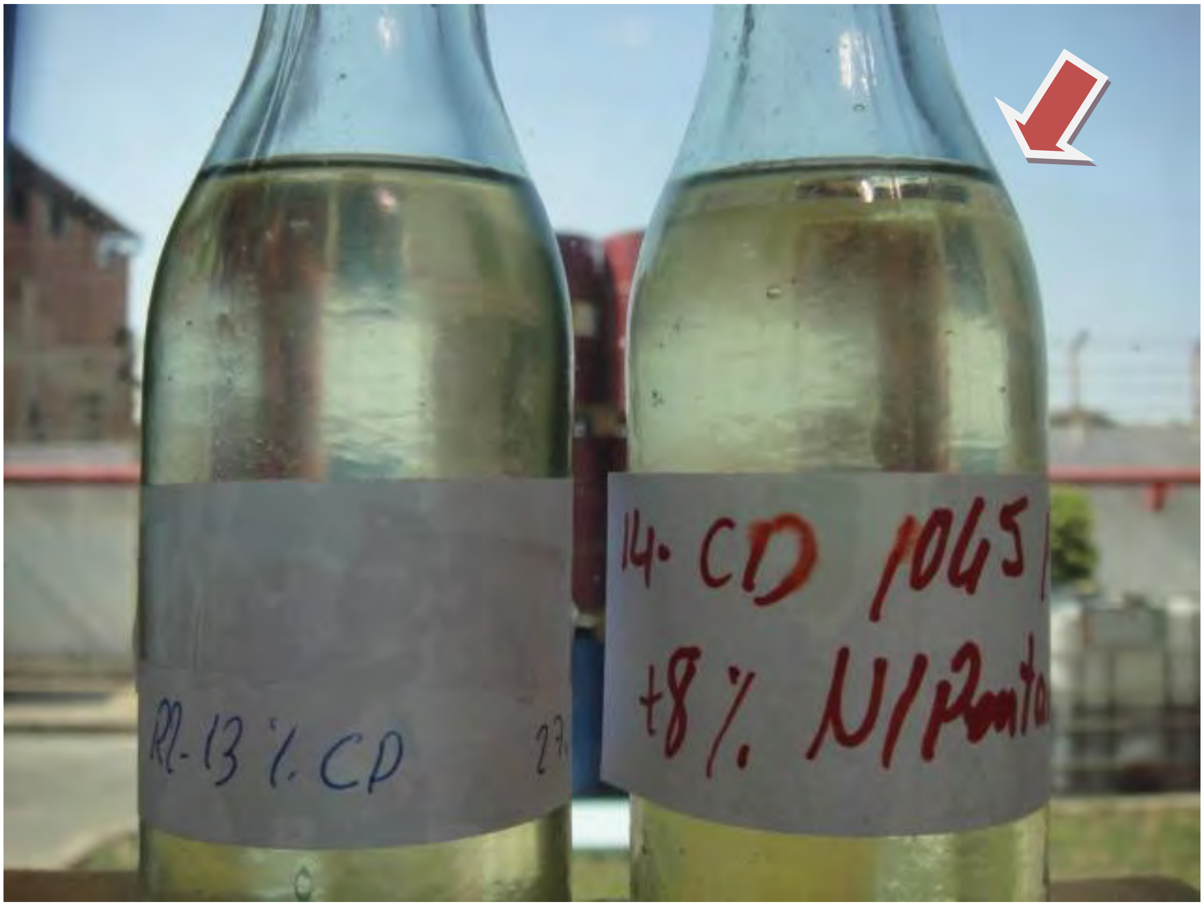


Chart 2: evolution of free rise density along time at 50°C aging temperature for polyol blend of System B fully formulated with c-pentane.

It is clear how the behavior of fully formulated blends would be not only formulation dependant but also handling and storing conditions highly dependent.

<u>n-pentane pre-blended polyols shelf- life.</u>

When considering n-pentane blown System D situation becomes more critical, and this specific system, which contains 8pbw n-pentane on top of 100pbw polyol , gave physical separation of n-pentane from the blend already after few weeks (see red arrow in the picture below), when instead the c-pentane blown System B was still stable .
Picture 12: 1 month aging physical stability of c-pentane in System B (on the left) and n-pentane in System D (on the right). Phase Separation of n-pentane is visible.


RR-13% CD
27.
14· CD 1045
+8% N/Penta

CONCLUSIONS

Outcome of this project according to initial objectives can be summarized as follows:

- NEW DISPENSING UNIT:
  - new high pressure dispensing unit, convertible from 2 component isocyanate/pre-blended hydrocarbon polyols use into 3 components isocyanate/polyol without pentane/third stream pentane addition directly in the mixing head , is validated to be working properly across the two type of injection process
- PRE-BLENDED HYDROCARBONS
  - Pre-blended hydrocarbons technology, as known in the literature and from industrial experience of various years , are confirmed to give a good pattern of foam properties.
  - Most standard practice today in the industry is foam manufacturer doing the pre-blend directly at its production site, which requires very limited shelf life of fully formulated polyol , with no particular criticality given proper formulation .
  - In a different scenario of pre-blending, where addition of hydrocarbons would take place already by system supplier, longer time pentane stability in the polyol blend would be required, typically 6 months shelf life, increasing criticality, especially in case of the less soluble pentane isomers.
  - Physical and chemical stability tests on fully formulated polyol blends containing pentane to predict a 6 months shelf life (still ongoing) indicate already that n-pentane System D is not suitable for extended pre-blend shelf life, while the c-pentane System B behave reasonably so far for a period of 3 months with 13 pbw pentane on top of 100 pbw polyol was used. It is recognized that shelf life is also dependant on formulation of specific system.
  - Future work: aging of fully formulated polyol with c-pentane will continue upon reaching 6 months and shelf life results will be reported. A tailored formulation with n-pentane will also be checked to complete assessment about criticality of n-pentane for a 6 months shelf life. Expectation is that in any case n-pentane blends would remain very critical, with impact on the level of physical blowing agent that can be kept stable in the polyol blend.
- THIRD STREAM
  - Third stream addition of pentane directly in the mixing head is confirmed to be working with good reproducibility and consistency across different injections duration, giving homogeneous results.
  - Future work: Optimization of pentane impingement pressure and reactivity will be done to close the delta in gel time and thermal conductivity that were observed vs pre-blended process
- HYDROCARBON vs HCFC141b EFFECTIVENESS:
  - The performance achievable with Hydrocarbon blown polyurethane systems, in comparison with HFCF 141b technologies in use in the Egyptian market, confirms “generation 1” hydrocarbon systems are effective alternative for polyurethane foam producers to move into Zero ODP (also low GWP) more sustainable solutions.
  - This comparison has to be considered valid for other countries as well
  - Hydrocarbon blown systems utilized in the workshop are already in use in developed countries, with successful track records.
- EH&S:

o The experiments within the scope of this project were performed in accordance with the recommendations from an Environmental, Health and Safety Risk Assessment.

o Replication of these experiments should only be performed after completing Environmental, Health and Safety Risk Assessment by a qualified professional.

o Reference to the Material Safety Data Sheets for Environmental, Health and Safety information on the substances used in this project and to dispensing unit documentation from equipment suppliers must be made.

o In particular, for Environmental, Health and Safety aspects relative to third stream pentane addition handling and storage connection, reference must be made to documentation from the equipment supplier.

Authors

Cecilia Girotti is Sr. Chemist R&D for Polyurethane Rigid Foams of Dow Formulated Systems and is located in Correggio, Italy. She joined Dow in 2002 and before her current position she was responsible for managing the physic-mechanical foam testing laboratory in Correggio. Cecilia has a MS in Chemistry from the University of Modena (Italy, 1999).

Francesca Pignagnoli is Global Business Development Leader for DOW Energy Efficiency Formulated Systems and is located in Correggio, Italy. She joined DOW in 1997 and before her current position she was Global Development leader managing R&D group for Rigid Polyurethane Systems. Francesca has a MS in Organic Chemistry from the University of Parma (Italy, 1995).

Mohammed El Fikky is Technical and Sales Representative for DOW Energy Efficiency Formulated Systems ad is located in Cairo, Egypt. He joined DOW in 1998 and before his current position he was responsible for the TS&D laboratory Supervisor, Mohamed has a B.Sc in Chemical Engineering from the Higher Technological Institute, 10th of Ramadan City (Egypt, 1996)

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Final update on shelf lives study for

Hydrocarbon blown polyurethane systems workshop in the field of UNDP project Egypt.

INTRODUCTION

Among proven Zero ODP blowing agent options, which include hydrocarbons, hydro-fluorocarbons and water, hydrocarbons are the most utilized, thanks to the good mix of performance features (final foam properties, processing window, cycle time) and low cost, in particular in the domestic appliance industry and continuous laminated sandwich panels industry, but not only. Still, part of the smaller producers in applications like for example commercial appliances, water heaters and discontinuous panels, face the limitation of the investment required to handle the flammability aspects.

Generally, in case of pentane based technologies, polyol blends are supplied without pentane to the foam manufacturers by system supplier and then foam manufacturers add themselves the pentane

- directly at the mixing head as third stream component (as in case of continuous production process)
- preblending it to the polyol component through a pre-mix unit (as in case of typical discontinuous process)

Pentane based solutions in discontinuous process

This type of operation typically does not require pentane to be stable in polyol blend for long time, and shelf life of polyol blends without pentane is not critical.
A different situation would be represented by a practice where the system supplier already pre-blends pentane in its polyol blend, and supplies it fully formulated to the foam manufacturer. In this case pentane would need to be stable in the polyol blend for some months, typically 3-6 months, which in principle is a quite critical situation especially for the less soluble pentane isomers like n-pentane, and extremely critical situation in case the suggested storage temperature conditions both during handling, shipping and storage are not fully respected. Of course the shelf life behavior is also formulation dependant.
Aim of this study has been to understand the impact of the addition of hydrocarbons on physical and chemical shelf life of polyols blends when considering a scenario of pre-blending done by the system supplier (longer shelf lives requested), and not by the foam producer.
Worth to mention that is this particular scenario, the topic of investing to handle flammability aspects and risks of pentane would be extended to a larger number of players, as supplier would have to invest to handle pentane in its operation, and as polyol blends containing pentane have flash point and are flammable materials, with additional costs upstream in the value chain to be sustained by suppliers, and that would reflect into system price.
Nevertheless, in order to understand the criticality of such scenario, shelf life of pre-blended polyol with pentane was studied for a prolonged time period to understand criticality.

The experimental program for data generation encompassed two different applications:

- commercial appliance
- discontinuous panels

and different pentane isomers:

- cyclo pentane (typically used in commercial appliance applications)
- normal pentane (typically used in discontinuous panel applications)

EXPERIMENTAL

Physical stability of the polyol blend

The evaluation of the blowing agents' physical stability in fully formulated polyols was performed by studying the total blend stability at room temperature along time. After properly mixing the fully formulated polyol with the blowing agent, 200 grams (0.44 lb) of the blend were poured into a glass bottle (capacity: 0.09 gal, 350 ml), visually monitoring phase separation at regular intervals.

Chemical stability of the polyol blend

The chemical stability of the polyol blends was evaluated by storing the fully formulated blends at room temperature and at 50°C, and by performing reactivity and free rise density measurements after specific time intervals. Glass bottles containing the fully formulated polyols were stored inside thermostatic baths kept at constant temperature (20 and 50°C respectively) under a walk-in suction hood. In order to minimize loss of pentane during the whole study a different glass bottle (sample) was used for each performance evaluation.

RESULTS AND DISCUSSION

System A: Cyclo-pentane based system for Commercial appliance

5 months aging of fully formulated polyol of system A, containing 13pbw of c-pentane on top of 100pbw of polyol, gave good physical stability with no c-pentane separation observed, as reported in Table 1 below.

Table1: physical stability of system A at room temperature

Test #	Initial	two weeks	4 weeks	6 weeks	8 weeks	20 weeks
Physical stability	No phase Separation	No phase Separation	No phase Separation	No phase Separation	No phase Separation	No phase Separation

Within the 5 months so far evaluated the chemical stability is almost ok, both at room and high temperature with only small acceleration of reactivity, as explained in Table 2 below. The system density remains constant versus time at both storing conditions.

Table2: chemical stability of system A

Test #	Initial	two weeks		4 weeks		6 weeks		8 weeks		20 weeks	
Temp.		50 °C	Room Temp.	50 °C	Room Temp.	50 °C	Room Temp.	50 °C	Room Temp.	50 °C	Room Temp.
Reactivity (Gel time, sec)	75	ok	ok	ok	ok	slightly faster	slightly faster	slightly faster	slightly faster	slightly faster	slightly faster
Free Rise Density (kg/m³)	30	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok

As a graphic example out of full data set, the reactivity and free rise density variations at both room and high storage temperatures are reported below.

Figure1: Systema A reactivity variation

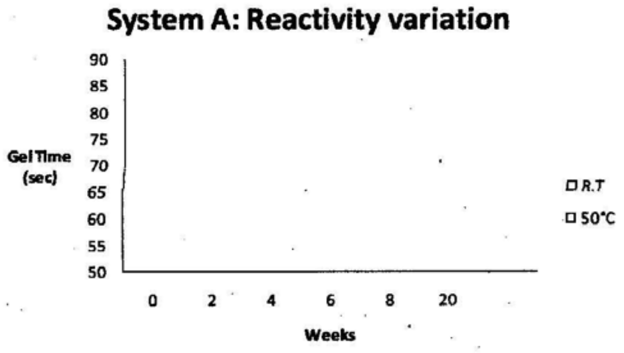
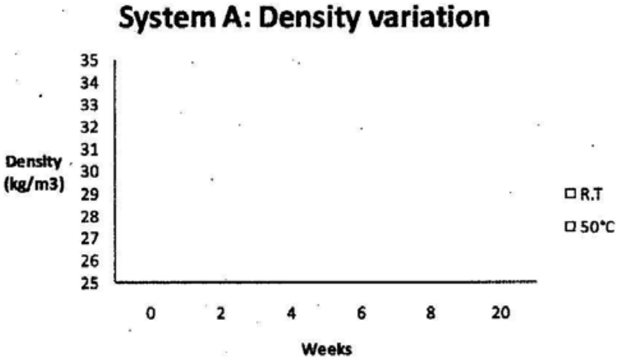


Figure 2: System A free rise density variation.



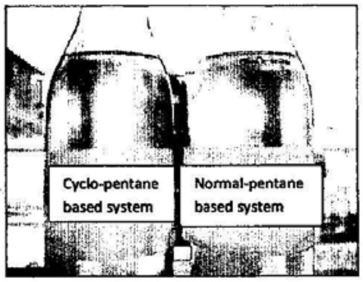
System B: Normal-pentane based system for Commercial appliance

Considering n-pentane based system the physical stability becomes more critical. System B, containing 8 pbw of n-pentane on top of 100 pbw of polyol, showed phase separation already after few weeks as reported in table 3 below.

Table3: physical stability of system B at room temperature

Test #	Initial	1 week	3 weeks	6 weeks	8 weeks	20 weeks
Physical stability	ok	N/A	N/A	Phase Separation	Phase Separation	Phase Separation

Picture 1: 1 month aging physical stability of c-pentane in System A (on the left) and n-pentane in System B (on the right). Phase Separation of n-pentane is visible (see the red arrow)



System B chemical stability was monitored only for 3 weeks as, after 1 months phase separation occurred. For 3 weeks system B showed constant reactivity and free rise density when stored at room temperature. At 50℃ a slightly density increase was observed already after 3 weeks.

Table4: chemical stability of system B

Test #	Initial	1 week		3 weeks	
Temp.		50 °C	Room Temp.	50 °C	Room Temp.
Reactivity (Gel time, sec)	125	ok	ok	ok	ok
Free Rise Density (kg/m^3)	32,2	ok	ok	slightly higher	ok

Aging of blends is still ongoing, at this stage we have reached 5 months for the c-pentane system tested, and we have stopped the aging of the n-pentane system for reasons reported below.

CONCLUSIONS

In conclusion , based on formulations studied and small scale tests performed, n-pentane does not appear to be a suitable blowing agent for pre-blended solutions with shelf life needs of some months.
On the contrary c-pentane demonstrated to be manageable in such scenario, provided that suggested storage conditions are respected.
Data generated are of course only indicative of real scale performance, which should be monitored in case an approach of supplying to manufacturers a fully pre-blended polyol with pentane is selected.

Third stream pentane addition technology has demonstrated, in straight comparison with traditional pre-blended pentane technology, to give slightly slower gel time reactivity. This change in reactivity has not impacted applied densities and productivity, while it has shown a small impact eventually on thermal conductivity . In case manufacturer has specific reasons to compensate this and completely offset reactivity difference, it is suggested to use a formulation with a slight adjustment of catalyst package in order to close the reactivity gap.