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COMITÉ EJECUTIVO DEL FONDO MULTILATERAL
PARA LA APLICACIÓN DEL
PROTOCOLO DE MONTREAL
Sexagésima sexta Reunión
Montreal, 16 – 20 de abril de 2012

# INFORME SOBRE LA EJECUCIÓN DE PROYECTOS APROBADOS CON REQUISITOS ESPECÍFICOS DE PRESENTACIÓN DE INFORMES

**Introducción**

1. La Secretaría pidió a los organismos bilaterales y de ejecución que presentaran a la 66ª reunión los informes pendientes sobre la marcha de las actividades de la ejecución de proyectos para los que se hubieran incluido requisitos de presentación de informes específicos en los acuerdos y en las decisiones pertinentes del Comité Ejecutivo adoptadas entre las reuniones 59ª y 65ª.

2. Este documento incluye informes para los siguientes países, que se presentaron después de la fecha límite de ocho semanas de antelación para la 65ª reunión y que la Secretaría no había podido examinar: Burkina Faso (informe de verificación del plan de gestión de eliminación definitiva); China (informes de progresos en el sector de solventes y de verificación); Côte d'Ivoire (informe de verificación del plan de gestión de eliminación definitiva); Indonesia (informe de verificación del plan nacional de eliminación); Kirguistán (informe sobre la marcha de las actividades del plan de gestión de eliminación definitiva); Santo Tomé y Príncipe (informe de verificación del plan de gestión de eliminación definitiva).

Estructura del documento

3. La Secretaría ha agrupado los informes sobre la marcha de las actividades en seis secciones:

Sección I: Planes nacionales de eliminación y planes de gestión de eliminación definitiva

Sección II: Planes de eliminación sectoriales

Sección III: Fortalecimiento institucional

Sección IV: Movilización de recursos para lograr cobeneficios climáticos

Sección VI: Proyectos de destrucción de SAO

Sección VI: Proyectos de demostración e inversión relacionados con HCFC

## I. PLANES NACIONALES DE ELIMINACIÓN Y PLANES DE GESTIÓN DE ELIMINACIÓN DEFINITIVA

4. El PNUD, el PNUMA, la ONUDI y el Banco Mundial han presentado los siguientes informes:

a) Brasil: plan nacional de eliminación de CFC (informe de verificación de 2010, informe sobre la marcha de las actividades de 2011 y plan de acción para 2012) (PNUD)

b) Burkina Faso: informe de verificación de la ejecución del plan de gestión de eliminación definitiva (2008) (PNUMA)

c) Côte d'Ivoire: informe de verificación de la ejecución del plan de gestión de eliminación definitiva (2007-2008) (PNUMA)

d) Indonesia: plan nacional de eliminación (verificación del desempeño de 2007-2008) (PNUD)

e) Kirguistán: informe sobre la marcha de las actividades de la ejecución del plan de gestión de eliminación definitiva (tercer y último tramo) (PNUMA)

f) Filipinas: plan nacional de eliminación de CFC (informes de verificación de 2009 y 2010 y plan de acción para 2012) (PNUMA)

g) Santo Tomé y Príncipe: informe de verificación de la ejecución del plan de gestión de eliminación definitiva (2007-2009) (PNUMA)

5. La Secretaría examinó los informes presentados tomando en cuenta las propuestas de proyecto originales, los datos de SAO notificados por los correspondientes gobiernos conforme al Artículo 7 del Protocolo de Montreal, los informes sobre la marcha de las actividades anteriores presentados al Comité Ejecutivo y las decisiones pertinentes adoptadas por el Comité Ejecutivo y la Reunión de las Partes.

**Brasil: plan nacional de eliminación de CFC (informe de verificación de 2010, informe sobre la marcha de las actividades de 2011 y plan de acción para 2012) (PNUD)**

6. El plan nacional de eliminación para eliminar completamente el consumo de CFC en el Brasil antes del 1 de enero de 2010 fue aprobado por el Comité Ejecutivo en la 37ª reunión, con un nivel de financiación aprobado en principio de 26.700.000 $EUA. El octavo y último tramo del plan nacional de eliminación fue aprobado por el Comité Ejecutivo en la 59ª reunión. El Comité también pidió la verificación anual del plan nacional de eliminación de CFC para el Brasil hasta que se hubiese presentado la verificación del consumo de 2010. En la 63ª reunión, el Comité Ejecutivo pidió al Gobierno de Brasil que, con la asistencia del PNUD, presentase informes de ejecución anuales respecto del año anterior a la primera reunión del Comité Ejecutivo cada año hasta que se hubiese completado el plan nacional de eliminación. El PNUD ha presentado a la 66ª reunión la verificación del consumo para el año 2010 y el informe sobre la marcha de las actividades de 2011, así como un plan de ejecución anual para 2012.

*Informe de verificación*

7. El informe de verificación demostró que el Brasil ha cumplido los requisitos del acuerdo entre el Gobierno del Brasil y el Comité Ejecutivo sobre la eliminación de CFC para 2010. En 2010 Brasil no registró importaciones y registró 13,8 toneladas PAO de exportaciones de CFC.

*Informe sobre la marcha de las actividades de 2011*

8. En el sector de servicio y mantenimiento de refrigeración, se distribuyó a mayor parte de los juegos de herramientas comprado. Se encuentra actualmente en funcionamiento un centro de regeneración en la región sur del Brasil (Porto Alegre) y se ha establecido la última planta de almacenamiento. Se instalaron 47 unidades de reciclaje en 2011, con lo que el total asciende a 95 unidades y resta instalar otras 25. Se seleccionaron dos edificios públicos que recibirán enfriadores que no utilizan CFC y se ha iniciado el proceso de licitación para la adquisición. Se seleccionaron cuatro establecimientos para la demostración de retroadaptaciones o sustituciones de equipos de refrigeración comercial, y se ha iniciado el proceso de adquisición. Finalmente, se ha distribuido un documental relativo a la transición de inhaladores de dosis medidas que contienen CFC a productos de alternativa, y se ha preparado un folleto.

*Plan de ejecución anual para 2012*

9. Para 2012, se prevén varias actividades para concluir el plan nacional de eliminación: establecimiento y puesta en funcionamiento de equipos para las 25 unidades de reciclaje de CFC-12 restantes en el norte del Brasil, junto con herramientas de recuperación para técnicos que también pueden utilizarse con HCFC y algunos HFC; puesta en funcionamiento de dos enfriadores sustitutivos en dos edificios públicos; retroadaptación o sustitución de otras 18 unidades de equipos comerciales que utilizan

CFC-12; finalización de una norma técnica sobre límites de ventilación de CFC; mejora del módulo nacional de comercio para el sistema de control de CFC para incorporar herramientas de seguimiento para refrigerantes recuperados, reciclados y regenerados localmente; y cierre operativo y financiero del proyecto.

Observaciones de la Secretaría

*Informe de verificación*

10. Los datos presentados en el informe de verificación guardan conformidad con los datos de consumo notificados con arreglo al Artículo 7 por el Brasil a la Secretaría del Ozono.

*Fondos aprobados y saldos*

11. A diciembre de 2011, se habían desembolsado todos los fondos excepto 1.808.548 $EUA (7%). El PNUD informó que el saldo restante ya se ha comprometido para actividades del plan nacional de eliminación. Dos actividades pueden tener posibles sinergias con las actividades relacionadas con los HCFC, pero no tendrán ninguna eliminación de HCFC asociadas; estas son las medidas de control de ventilación/emisiones de CFC y la mejora de la gestión de las reservas originadas por la recuperación. En la medida posible, estas sinergias se han tenido en cuenta en el plan de gestión de eliminación de los HCFC para el Brasil aprobado en la 64ª reunión.

*Plan de ejecución anual para 2012*

12. La Secretaría también pidió información adicional sobre los equipos que se están comprando para empresas pequeñas y medianas del sector de refrigeración comercial. El PNUD informó que los equipos se basarán en tecnologías que no utilizan SAO.

13. La Secretaría señaló que el informe sobre la marcha de las actividades también incluía dados sobre centros de recuperación y reciclaje y centros de regeneración de HCFC-22 y CFC que indican que en 2011 los centros han procesado menores cantidades de CFC-12 y HCFC-22 que en 2009. La cantidad de CFC-12 procesado en los centros de regeneración parece haber disminuido de 4,8 toneladas PAO en 2010 a 2,9 toneladas en 2011, mientras que el HCFC-22 ha aumentado a 27,4 toneladas en 2011, en comparación con 16,9 toneladas en 2010. La tasa de recuperación más baja de CFC-12 puede deberse a la sustitución de equipos de refrigeración así como al hecho de que los propietarios de grandes equipos industriales a base de CFC-12 parecen estar acumulando reservas de CFC para fines de mantenimiento. El aumento en las tasas de recuperación y regeneración de HCFC se relaciona con los límites impuestos por el Gobierno del Brasil al aumento del consumo de HCFC en el contexto de su plan de gestión de eliminación de los HCFC. Los precios del HCFC-22 virgen han aumentado alrededor del 30% al 40% y, por lo tanto, las actividades de recuperación y reciclaje de HCFC-22 han resultado más viables desde el punto de vista económico.

14. El PNUD proporcionó información adicional en respuesta a un pedido de más detalles acerca de la medida en que las actividades planificadas para 2012 podrían contribuir a mantener un consumo nulo de CFC y facilitar la eliminación de los HCFC en el Brasil. En el Brasil, los CFC están disponibles únicamente a través de la estructura de actividades de sustitución de equipos, recuperación, reciclaje y regeneración. Esta estructura proporciona CFC reciclados/regenerados de alta calidad para los equipos hasta que los propietarios estén listos (desde el punto de vista económico o técnico) para sustituir o retroadaptar los equipos que funcionan a base de CFC. Los CFC recuperados de la sustitución de enfriadores y equipos comerciales pequeños se pueden reciclar no solo para asegurar una transición sin problemas y reducir el riesgo del comercio ilícito, sino también para proporcionar una alternativa rentable

a la ventilación a la atmósfera de CFC de alto potencial de calentamiento atmosférico (PCA). La estructura de recuperación, reciclaje y regeneración instalada también puede manejar HCFC y algunos HFC. La finalización de una norma técnica sobre los límites de ventilación de CFC a la atmósfera en el sector de refrigeración comercial también incluirá límites de ventilación a la atmósfera para los HCFC. La mejora del "módulo de comercio nacional de CFC" proporcionará una herramienta de seguimiento para los refrigerantes recuperados, reciclados y regenerados. Esta herramienta supervisa el comercio nacional, proporciona información oportuna a las autoridades y se puede reproducir para la supervisión de los HCFC y HFC.

Recomendación de la Secretaría

15. El Comité Ejecutivo pudiera considerar:

a) Tomar nota del informe de verificación para 2010 y del informe anual de ejecución de 2011 del plan nacional de eliminación de CFC en el Brasil;

b) Aprobar el plan anual de ejecución para 2012; y

c) Pedir al PNUD que continúe notificando los progresos en la ejecución del plan nacional de eliminación en el Brasil, proporcionando además otros informes en un formato y con un calendario que guarden conformidad con los resultados de las deliberaciones mantenidas en el contexto de la cuestión 7 d) del orden del día; y

d) Pedir al Gobierno del Brasil y al PNUD que, una vez que se haya completado el plan nacional de eliminación, presenten un informe de terminación de proyecto conforme al formato indicado en la 65ª reunión.

**Burkina Faso: informe de verificación de la ejecución del plan de gestión de eliminación definitiva (2008) (PNUMA)**

*Antecedentes*

16. En nombre del Gobierno de Burkina Faso, el PNUMA, como organismo principal, ha presentado una verificación del consumo de CFC en dicho país para 2008 conforme a la decisión 45/54 d). El plan de gestión de eliminación definitiva para Burkina Faso fue aprobado por el Comité Ejecutivo en la 50ª reunión para eliminar completamente el consumo de CFC en el país antes del 1 de enero de 2009. El Comité Ejecutivo aprobó en principio una financiación total de 345.000 $EUA, más costos de apoyo al organismo de 23.400 $EUA para el PNUMA y de 21.450 $EUA para el Gobierno del Canadá, que se liberaron a cada organismo en dos tramos en las reuniones 50ª y 54ª del Comité Ejecutivo.

*Informe de verificación*

17. La verificación demostró que no hubo consumo de CFC en Burkina Faso en 2008 y que el sistema de otorgamiento de licencias para las SAO estaba funcionando bien. Se comprobó que le consumo de HFC-134a y HCFC-22 estaba disminuyendo. El informe indicó que Burkina Faso cuenta con un reglamento sólido y eficiente para controlar las SAO y que, desde enero de 2006, también ha estado en vigor un reglamento subregional que cubre la Unión Económica y Monetaria del África Occidental (UEMOA) (Burkina Faso, Benin, Côte d'Ivoire, Gambia, Malí, Senegal y Togo) que prohíbe la importación y exportación de todas las sustancias de los Anexos A, B y E y los equipos que las contienen.

Observaciones de la Secretaría

18. El Gobierno de Burkina Faso ha notificado un consumo nulo de CFC con arreglo al Artículo 7 del Protocolo de Montreal para los años 2008, 2009 y 2010.

19. El PNUMA informó a la Secretaría que el reglamento de la UEMOA aún no se ha enmendado para prohibir los HCFC; no obstante, actualmente incluye el otorgamiento de licencias para la importación de HCFC y equipos que funcionan a base de HCFC.

20. La Secretaría observó que el informe de verificación contenía una recomendación de analizar los reglamentos existentes a fin de que tomen en cuenta los HCFC y los equipos que funcionan a base de HCFC. El PNUMA explicó que se ha presentado al gobierno un nuevo proyecto de reglamento para introducir cuotas anuales desde 2013 para su aval, dado que los reglamentos actuales (nacional y subregional) solamente requieren que se emita un permiso de importación, pero no incluyen ninguna restricción de la cantidad permitida.

Recomendación de la Secretaría

21. El Comité Ejecutivo pudiera:

a) Tomar nota del informe de verificación del consumo de CFC para Burkina Faso y del cumplimiento del país de sus obligaciones de eliminación respecto del consumo de CFC; y

b) Tomar nota asimismo con satisfacción de que Burkina Faso ha notificado un consumo nulo de CFC con arreglo al Artículo 7 del Protocolo de Montreal desde 2008.

**Côte d'Ivoire: informe de verificación de la ejecución del plan de gestión de eliminación definitiva (2007-2008) (PNUMA)**

*Antecedentes*

22. En nombre del Gobierno de Côte d'Ivoire, el PNUMA, como organismo principal, ha presentado una verificación del consumo de CFC en dicho país para 2007 a 2008 conforme a la decisión 45/54 d). El plan de gestión de eliminación definitiva para Côte d'Ivoire fue aprobado por el Comité Ejecutivo en la 54ª reunión para eliminar completamente el consumo de CFC antes de 2009. Se aprobó en principio una financiación total de 565.000 $EUA, más costos de apoyo al organismo de 36.660 $EUA para el PNUMA y de 21.225 $EUA para la ONUDI, que se liberaron a cada organismo en dos tramos en las reuniones 54ª y 58ª del Comité Ejecutivo.

*Informe de verificación*

23. La verificación demostró que Côte d'Ivoire alcanzó los objetivos generales de reducción del consumo de SAO a nivel nacional para 2008. El consumo real de SAO de 2008 fue de 20 toneladas PAO en comparación con el nivel máximo permitido de 44,1 toneladas PAO conforme a su acuerdo con el Comité Ejecutivo. En 2007, se determinó que el consumo de SAO había sido de 50 toneladas PAO. Junto con otros países de la subregión, el Gobierno de Côte d'Ivoire ha adoptado el reglamento de la UEMOA. El sistema de otorgamiento de licencias está funcionando bien y los órganos del gobierno pertinentes se comunican de manera eficaz.

Observaciones de la Secretaría

24. El Gobierno de Côte d'Ivoire ha notificado 35,5, 12,0, 12,0 y cero tonelada PAO de consumo de CFC con arreglo al Artículo 7 del Protocolo de Montreal para 2007, 2008, 2009 y 2010 respectivamente.

25. La Secretaría observó importantes diferencias entre los datos notificados conforme al Artículo 7 para 2007 y 2008 y los datos sobre importaciones del informe de verificación. En 2007, se notificó un consumo de CFC de 50 toneladas PAO en el informe de verificación en comparación con las 35,5 toneladas PAO notificadas con arreglo al Artículo 7, y en 2008 los datos respectivos fueron 20,0 toneladas PAO en comparación con 12,0 toneladas PAO. El PNUMA informó a la Secretaría que la dependencia nacional del ozono indicó que el informe de verificación contiene los datos más exactos y que había convenido en rectificar los datos ya notificados con arreglo al Artículo 7. El Gobierno de Côte d'Ivoire, con asistencia del PNUMA, presentó una nota oficial a la Secretaría del Ozono el 15 de marzo de 2011 pidiendo que se cambiara su consumo de CFC notificado con arreglo al Artículo 7 para los años 2007 y 2008.

Recomendación de la Secretaría

26. El Comité Ejecutivo pudiera:

a) Tomar nota del informe de verificación del consumo de CFC en Côte d'Ivoire y del cumplimiento del país de sus obligaciones de eliminación del consumo de CFC conforme al plan de gestión de eliminación definitiva para el período de 2007 a 2008 y de que el país ha notificado un consumo nulo de CFC en 2010.

b) Tomar nota de la solicitud del Gobierno de Côte d'Ivoire a la Secretaría del Ozono de cambiar sus datos de consumo de CFC notificados con arreglo al Artículo 7 para los años 2007 y 2008.

**Indonesia: plan nacional de eliminación (verificación del desempeño de 2007-2008) (PNUD)**

*Antecedentes*

27. El plan nacional de eliminación para Indonesia fue aprobado en la 44ª reunión del Comité Ejecutivo, con el PNUD como organismo de ejecución principal y la ONUDI y el Banco Mundial como organismos de ejecución cooperantes, para eliminar completamente el uso controlado de CFC, CTC y 1,1,1-tricloroetano (TCA) antes del 1 de enero de 2008. El plan nacional de eliminación para Indonesia consistía en una combinación de varios planes sectoriales anteriores y nuevas actividades e introdujo la verificación del consumo a nivel nacional. Los fondos aprobados para actividades del plan nacional de eliminación en seis tramos, desde la 37ª reunión hasta la 54ª reunión, ascendieron a 20.645.507 $EUA más costos de apoyo de organismo de 1.754.701 $EUA.

*Informe de verificación*

28. La verificación, llevada a cabo desde julio hasta agosto de 2009, demostró que Indonesia ha logrado los objetivos generales para el consumo de SAO a nivel nacional para 2007 y 2008, con un consumo real de SAO de 202,56 toneladas PAO y hasta 3,32 toneladas PAO en 2007 y 2008 respectivamente. Se cumplieron los objetivos de consumo de SAO para todos los sectores (espumas, servicio y mantenimiento de acondicionadores de aire de vehículos, fabricación de refrigeración, servicio y mantenimiento de refrigeración, aerosoles y solventes) en 2008 y para todos los sectores excepto el sector de acondicionadores de aire de vehículos en 2007. También se notificó que se ejecutaron de

manera completa todas las actividades relacionadas con políticas y reglamentos y aumento de la sensibilización en todos los sectores.

Observaciones de la Secretaría

29. El Comité Ejecutivo, al aprobar el último tramo del plan nacional de eliminación para Indonesia, estipuló la condición de que el PNUD como organismo de ejecución principal continuaría proporcionando, en nombre del gobierno, informes anuales y verificaciones del consumo de CFC durante el período restante del Acuerdo; es decir, para cubrir los años hasta 2010 inclusive. Los informes de verificación para 2009 y 2010 se encuentran actualmente pendientes, como así los informes de ejecución anuales para 2008, 2009, 2010 y 2011. El PNUD señaló que Indonesia prohibió la importación de CFC, CTC, 1,1,1-tricloroetano y halones a partir del 1 de enero de 2008, con antelación al calendario del Protocolo de Montreal, y que la verificación realizada para 2008 confirmó el cumplimiento de las condiciones del acuerdo con el Comité Ejecutivo. Los datos presentados por Indonesia con arreglo al Artículo 7 del Protocolo de Montreal indican un consumo nulo de SAO (diferentes de los HCFC) para los años 2008, 2009 y 2010. El PNUD indicó que no se realizaron actividades importantes en 2009 y 2010, excepto supervisión, y que el presupuesto restante de aproximadamente 16.000 $EUA se había programado para concluir las actividades en 2012.

30. La Secretaría señaló el hecho de que el verificador solamente pudo verificar el consumo de 2008 de manera aproximada, en alrededor de 3,32 toneladas PAO o menos, debido a discrepancias entre los datos de la aduana (0 tonelada PAO), la información del Ministerio de Comercio (0 tonelada PAO) y la información de la Oficina de estadísticas (3,32 toneladas PAO). Los datos de la Oficina de estadísticas se generaron sobre la base de registros de la aduana tanto escritos como electrónicos proporcionados a dicha oficina por 28 oficinas de aduanas. El verificador examinó el asunto y determinó que la discrepancia parece provenir de los registros escritos. La Secretaría señaló al PNUD que el Gobierno de Indonesia había notificado un consumo nulo de CFC con arreglo al Artículo 7 para el año 2008 y pidió aclaraciones. El PNUD explicó que el verificador, usando datos comparativos de diversas fuentes, identificó 3,32 toneladas PAO de importaciones en los datos de la Oficina central de estadísticas de Indonesia, mientras que no encontró importaciones en otras dos fuentes de datos; sin embargo, generalmente se pide al gobierno que use, en caso de discrepancias, los datos de las aduanas como fuente más confiable, y estos indican un consumo nulo. Por lo tanto, se mantendrán los datos notificados con arreglo al Artículo 7.

31. Las verificaciones confirman que Indonesia ha cumplido con el Acuerdo entre el gobierno y el Comité Ejecutivo acerca de la eliminación de los CFC en Indonesia, y que el consumo del país para 2007 y 2008 ha sido inferior al consumo máximo permitido especificado en dicho Acuerdo.

Recomendación de la Secretaría

32. El Comité Ejecutivo pudiera:

a) Tomar nota del informe de verificación del consumo de SAO para 2007-2008 en Indonesia;

b) Pedir al PNUD que, en nombre del Gobierno de Indonesia, presente los informes de verificación para 2009 y 2010 a la 68ª reunión; y

c) Pedir al PNUD que notifique los progresos en la ejecución del plan nacional de eliminación para Indonesia como sigue:

i) Para los años 2008 a 2011 a la 67ª reunión, proporcionando estos informes conforme a los resultados de las deliberaciones en el contexto de la cuestión 7 d) del orden del día; y

ii) Para el año 2012 y años futuros, proporcionando dichos informes en un formato y con un calendario conforme a los resultados de las deliberaciones en el contexto de la cuestión 7 d) del orden del día.

d) Pedir al Gobierno de Indonesia y al PNUD que, una vez que se haya completado el plan nacional de eliminación, presenten un informe de terminación de proyecto conforme al formato indicado en la 65ª reunión.

**Kirguistán: informe sobre la marcha de las actividades de la ejecución del plan de gestión de eliminación definitiva (tercer y último tramo) (PNUMA)**

33. El plan de gestión de eliminación definitiva para Kirguistán fue aprobado en principio en la 50ª reunión del Comité Ejecutivo, por un valor total de 550.000 $EUA y costos de apoyo al organismo de 54.065 $EUA para el PNUD y el PNUMA como organismos de ejecución. Toda la financiación prevista fue aprobada en tres tamos en las reuniones 50ª, 55ª y 60ª. En la 60ª reunión, se pidió al Gobierno de Kirguistán que presentase un informe sobre el programa de trabajo relacionado con el tercer y último tramo del plan de gestión de eliminación definitiva.

*Informe sobre la marcha de las actividades*

34. Desde que se aprobó el tercer tramo en abril de 2010, se han realizado varios talleres y seminarios en diferentes lugares de Kirguistán, que incluyen: tres talleres regionales de recuperación y reciclaje en 2010 (92 participantes); cinco talleres sobre prácticas óptimas en refrigeración en 2010 y 2011 (115 participantes); nueve talleres para impartir capacitación a funcionarios de aduanas e inspectores ambientales (265 funcionarios capacitados); y siete talleres sobre inhaladores de dosis medidas realizados en hospitales en 2010 (261 participantes). Además, 77 funcionarios de aduanas de Kirguistán participaron en dos talleres regionales realizados en el país en cooperación con el proyecto de aplicación para Europa y Asia Central (ECA). Se adquirió una unidad de recuperación y analizador de gases múltiples que se entregó a la Asociación nacional de refrigeración.

Observaciones de la Secretaría

35. Kirguistán notificó un consumo nulo de CFC en 2010 con arreglo al Artículo 7 del Protocolo de Montreal. A diciembre de 2011, se habían desembolsado todos los fondos aprobados para el plan de gestión de eliminación definitiva.

36. En la 63ª reunión, la Secretaría señaló que el enfoque inicial de la etapa I del plan de gestión de eliminación de los HCFC para Kirguistán será asegurar que se proporcionen equipos y herramientas de recuperación de refrigerantes adicionales para apoyar la capacitación de técnicos, dado que se calculaba que menos del 50% de estos contaban con capacidades básicas de reciclaje adecuadas (documento UNEP/OzL.Pro/ExCom/63/37). En respuesta a una pregunta de la Secretaría acerca de si las actividades realizadas en 2010 y 2011 en el contexto del plan de gestión de eliminación definitiva habían mejorado esta situación, el PNUMA respondió que la mayoría de los equipos comprados, excepto aquellos comprados en la última ronda de adquisiciones en el contexto del plan de gestión de eliminación definitiva, están ahora desactualizados en comparación con las herramientas avanzadas disponibles actualmente. Los organismos de ejecución informaron que algunos centros serían modernizados como parte del plan de gestión de eliminación de los HCFC; actualmente, parece poco probable que la

financiación relacionada con el plan de gestión de eliminación de los HCFC sea suficiente para actualizar todos los centros.

37. El PNUMA proporcionó algunas aclaraciones acerca de las cantidades de CFC-12 recuperado y reciclado en Kirguistán (véase el Cuadro 1). Del total de 18.973 kg de CFC recuperados en Kirguistán, 6.455 kg fueron reciclados por centros de recuperación y reciclaje en total entre 2003 y 2011.

**Cuadro 1: Cantidades de CFC recuperados y reciclados en Kirguistán**

| Año | Recuperados y reutilizados (filtrado en el sitio) (kg) | Reciclados y purificados por centros de recuperación y reciclaje (kg) |
|---|---|---|
| **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 |
| **Total** | **18 973** | **6 455** |

38. La dependencia nacional del ozono de Kirguistán confirmó que hay cinco unidades de recuperación y reciclaje para cubrir todo el país. Tres unidades, compradas en 2003 por medio de las actividades del plan de gestión de refrigerantes, pueden reciclar solamente CFC, mientas que las otras dos unidades, compradas durante la ejecución del plan de gestión de eliminación definitiva, pueden reciclar CFC y HCFC. Actualmente, no se reciclan HCFC en Kirguistán debido a la falta de incentivos dado que el costo del HCFC-22 virgen todavía es muy bajo.

Recomendación de la Secretaría

39. El Comité Ejecutivo pudiera:

a) Tomar nota del informe del programa de trabajo para 2010-2011 relacionado con el tercer y último tramo del plan de gestión de eliminación definitiva para Kirguistán;

b) Pedir al PNUMA que continúe notificando los progresos en la ejecución del plan de gestión de eliminación definitiva para Kirguistán, proporcionando además otros informes en un formato y con un calendario que guarden conformidad con los resultados de las deliberaciones mantenidas en el contexto de la cuestión 7 d) del orden del día; y

c) Pedir al Gobierno de Kirguistán y al PNUMA que, una vez que se haya completado el plan de gestión de eliminación definitiva, presenten un informe de terminación de proyecto conforme al formato indicado en la 65ª reunión.

**Filipinas: plan nacional de eliminación de CFC (informes de verificación de 2009 y 2010 y plan de acción para 2012) (PNUMA)**

*Antecedentes*

40. El plan nacional de eliminación de CFC para Filipinas se aprobó, en principio, en la 38ª reunión del Comité Ejecutivo celebrada en noviembre de 2002, por un monto total de 10.575.410 $EUA, más costos de apoyo al organismo de 896.788 $EUA, para eliminar 2.017,6 toneladas PAO de CFC. El primer tramo de 3.010.873 $EUA más costos de apoyo al organismo de 259.979 $EUA también fue convenido en la misma reunión. Los siguientes tramos se aprobaron posteriormente en las reuniones 41ª, 44ª, 47ª, 51ª y 54ª para financiar actividades desde 2003 hasta 2008.

41. En la 65ª reunión, el Comité Ejecutivo aprobó la transferencia de las actividades restantes del plan nacional de eliminación del Banco Mundial al PNUMA. En la decisión 65/10 e) se estipuló, entre otras cosas, que el Banco Mundial devolvería el saldo restante del plan nacional de eliminación a la 66ª reunión, y que el Gobierno de Filipinas, con la asistencia del PNUMA, presentaría a la 66ª reunión un informe de verificación sobre el consumo de CFC para 2009 y 2010 y un plan de ejecución para 2012-2013 para los fondos restantes del plan nacional de eliminación.

*Informe de verificación*

42. El consumo de CFC verificado sobre la base de las importaciones reales de 2009 fue de 208,64 toneladas PAO y cero tonelada PAO para 2010, en comparación con el consumo máximo permitido de 300 toneladas PAO y cero tonelada PAO para 2009 y 2010 respectivamente. Los datos notificados con arreglo al Artículo 7 del Protocolo de Montreal muestran que el consumo de CFC del país para 2009 y 2010 fue de 208,64 toneladas PAO y cero tonelada PAO respectivamente.

*Informe sobre la marcha de las actividades*

43. No se llevaron a cabo o completaron actividades nuevas en relación con la información presentada en la 65ª reunión, en la que se presentó un informe sobre la marcha de las actividades acumulativo hasta septiembre de 2011 inclusive. La única actividad adicional del informe fue la visita de un consultor en octubre de 2011 para finalizar la preparación de proyecto para el plan para el sector de espumas del plan de gestión de eliminación de los HCFC.

44. A finales de 2011 se había desembolsado el 82% (8.671.836 $EUA) de los 10.575.410 $EUA aprobados para el plan nacional de eliminación. El saldo restante (1.878.851 $EUA) se transferirá al PNUMA, como nuevo organismo de ejecución, en la 66ª reunión.

*Plan de ejecución para abril de 2012 a diciembre de 2013*

45. El PNUMA presentó, en nombre del Gobierno de Filipinas, un plan de ejecución para el saldo restante del proyecto a fin de sostener la eliminación de los CFC en el país y de asegurar que el consumo continúe siendo nulo. La mayoría de estas actividades son una continuación de aquellas iniciadas en años anteriores, e incluyen:

a) Supervisión continua de los beneficiarios de donaciones y de otras empresas enumeradas en el plan nacional de eliminación (empresas de espumas y refrigeración) a fin de garantizar que cumplan con lo estipulado;

b) Entrega de equipos al centro de capacitación para técnicos de servicio, incluyendo apoyo continuo para la certificación de técnicos a fin de incluir el servicio y mantenimiento de equipos que funcionan con HCFC;

c) Asistencia técnica continua para inspección de equipos de aire acondicionado de vehículos para sostener la aplicación de la importación de vehículos con equipos de aire acondicionado que utilizan CFC-11 proporcionando identificadores de refrigerantes a los puestos de inspección;

d) El desarrollo de un sistema de gestión de la información que vincule a las diferentes instituciones que participan en la ejecución del plan nacional de eliminación para supervisar los progresos de las actividades;

e) Terminación del sistema de comprobantes y distribución de las herramientas y equipos restantes para el servicio adecuado de refrigeradores y acondicionadores de aire, así como finalización de la auditoría técnica de este sistema;

f) Apoyo operativo adicional a las oficinas de gestión ambiental regionales para asegurar la ejecución de actividades en el sector de servicio y mantenimiento en todo el país;

g) Fortalecimiento de la cooperación y coordinación interinstitucional regional proporcionando vínculos de información;

h) Suministro de las herramientas restantes a las plantas de regeneración y aplicación del programa de regeneración de desechos de SAO;

i) Aumento de la sensibilización continuo; y

j) Continuación del funcionamiento de la unidad de gestión de proyecto para coordinar estas actividades.

46. En su ponencia, el Gobierno de Filipinas pidió contar con autoridad para continuar con la terminación de todos los proyectos del plan nacional de eliminación hasta diciembre de 2013 y comprometer completamente los fondos restantes para el proyecto durante este período.

47. El presupuesto para el plan de ejecución para 2012-2013 se resume en el Cuadro 2 a continuación (el presupuesto detallado se adjunta como Anexo I); este incluye el monto solicitado para financiación retroactiva, de 43.080 $EUA, para gastos incurridos entre julio y diciembre de 2011:

**Cuadro 2: Resumen del plan de trabajo y presupuesto propuestos**

| **Abril de 2012 – Diciembre de 2013** | **Presupuesto ($EUA)** |
|---|---:|
| Gestión de proyecto | 604 172 |
| Prevención de oferta adicional de SAO/HCFC | 259 525 |
| Eliminación de demanda de CFC en el país | 510 823 |
| Gestión de las SAO no deseadas | 198 593 |
| Información, educación y comunicación y sensibilización del público | 305 738 |
| **Total** | **1 878 851** |

Observaciones de la Secretaría

48. La Secretaría examinó el plan de trabajo presentado por el Gobierno de Filipinas por conducto del PNUMA conforme a los planes de trabajo anteriores para el plan nacional de eliminación, y las medidas restantes requeridas para sostener la eliminación de los CFC en el país. Según los datos notificados con arreglo al Artículo 7 para 2010 y el informe de verificación presentado, Filipinas ha alcanzado los objetivos de cumplimiento del Protocolo de Montreal para los CFC. Considerando que hay un saldo restante de casi el 20% de los fondos para el plan nacional de eliminación (véase el párrafo 44 *supra*) y que no hay objetivos de eliminación de SAO vinculados con el plan de trabajo, el progreso se debería supervisar para cada actividad, conforme a las actividades específicamente identificadas y convenidas por el Comité Ejecutivo.

49. La Secretaría señaló que la mayoría de las actividades enumeradas eran actividades incompletas de los planes de trabajo del plan nacional de eliminación desde 2007 hasta 2009, y que no todas las actividades tenían en cuenta actividades de eliminación de HCFC, especialmente aquellas en el sector de servicio y mantenimiento (p. ej., capacitación y trabajo con técnicos de servicio). La Secretaría, además, llamó a la atención del PNUMA el hecho de que si bien puede ser necesario ejecutar actividades para sostener un consumo nulo de CFC, el Comité Ejecutivo había aclarado que los fondos restantes para la eliminación de los CFC debían tener en cuenta actividades que facilitasen la eliminación de los HCFC. La Secretaría también expresó preocupación por el hecho de que una gran cantidad de actividades relacionadas con la eliminación del plan de trabajo actualmente propuesto para 2012 y 2013 no estaban justificadas con claridad.

50. En su respuesta, el PNUMA notificó a la Secretaría que Filipinas había sufrido algunas demoras en la ejecución de actividades que había planificado anteriormente debido a dificultades con los desembolsos y a la terminación del acuerdo de donación anterior con el Banco Mundial, del que aún quedaban actividades pendientes. La transición a un nuevo organismo de ejecución también necesitaba ajustes en los arreglos financieros y de ejecución que también contribuían a esta situación. El PNUMA también indicó que el plan de trabajo actual tenía en cuenta los compromisos financieros que había contraído Filipinas con sus asociados para la eliminación de los CFC, que debían completarse dado que estos serían los mismos asociados para la eliminación de los HCFC.

51. La Secretaría, considerando la justificación proporcionada, propuso que el plan de trabajo actual podría cubrir los compromisos inmediatos para los próximos 12 meses solamente, pero por un monto menor que aquel propuesto en el Cuadro 2 *supra*, incluida la financiación retroactiva solicitada. También llamó a la atención del PNUMA el hecho de que la estrategia general del plan de gestión de eliminación de los HCFC para Filipinas estaba aún pendiente, e indicó que el Gobierno de Filipinas debería agilizar su terminación tomando en cuenta los fondos restantes del plan nacional de eliminación, y considerar seriamente cómo se podrían integrar en el plan de gestión de eliminación de los HCFC, especialmente para el sector de servicio y mantenimiento. Se podría considerar el desembolso del saldo restante una vez que el Comité Ejecutivo hubiera aprobado un plan de trabajo anual de ejecución futuro. El Gobierno de Filipinas y el PNUMA presentaron un presupuesto revisado para los 12 meses siguientes que se presenta en el Cuadro 3 a continuación:

**Cuadro 3: Plan de trabajo y presupuesto convenidos para abril de 2012 a abril de 2013**

| Abril de 2012 – Abril de 2013 | Presupuesto ($EUA) |
|---|---|
| Prevención de oferta adicional de SAO/incluidos los HCFC | 65 000 |
| Continuación de la labor en el sector de servicio y mantenimiento (prevención de demanda adicional de CFC, incluidos los HCFC) | 170 000 |
| Gestión de las SAO no deseadas | 30 000 |
| Sensibilización y difusión de información | 20 000 |
| Unidad de gestión de proyecto | 143 550 |
| ***Subtotal*** | ***428 550*** |
| Financiación retroactiva (julio de 2011 a diciembre de 2011) | 43 080 |
| **Total** | **471 630** |

Recomendación de la Secretaría

52. El Comité Ejecutivo pudiera considerar:

a) Tomar nota:

i) Del informe de verificación del consumo de CFC de 2009 y 2010 en Filipinas y del cumplimiento del país de sus obligaciones de eliminación para el consumo de CFC;

ii) De que Filipinas había notificado un consumo nulo de CFC con arreglo al Artículo 7 del Protocolo de Montreal para 2010;

iii) Del plan de ejecución anual del plan nacional de eliminación de CFC para abril de 2012 a abril de 2013 presentado por el PNUMA en nombre del Gobierno de Filipinas, y aprobar las actividades contenidas en dicho plan para el desembolso de no más de $471,630 para este período, y pedir al PNUMA que presente un informe anual al Comité Ejecutivo acerca de los progresos logrados en la 70ª reunión, con un formato que guarde conformidad con las deliberaciones mantenidas en el contexto de la cuestión 7 d) del orden del día; y

b) Pedir al Gobierno de Filipinas que por conducto del PNUMA presente un plan de trabajo anual subsiguiente para el saldo restante de 1.407.221 $EUA a más tardar en la 68ª reunión del Comité Ejecutivo, tomando en cuenta que los fondos restantes deberían considerar actividades que faciliten la eliminación de los HCFC dentro del contexto del plan de gestión de eliminación de los HCFC del país.

**Santo Tomé y Príncipe: informe de verificación de la ejecución del plan de gestión de eliminación definitiva (2007-2009) (PNUMA)**

*Antecedentes*

53. En nombre del Gobierno de Santo Tomé y Príncipe, el PNUMA, como organismo principal, ha presentado una verificación del consumo de CFC en dicho país para el período de 2007 a 2009 conforme a la decisión 45/54 d). El plan de gestión de eliminación definitiva para Santo Tomé y Príncipe fue aprobado por el Comité Ejecutivo en la 54ª reunión para eliminar completamente el consumo de CFC en

el país antes de 2009. El Comité Ejecutivo aprobó en principio una financiación total de 190.000 $EUA, más costos de apoyo al organismo de 9.750 $EUA para el PNUMA y de 10.350 $EUA para la ONUDI, que se liberaron a los organismos en dos tramos en las reuniones 54ª y 57ª del Comité Ejecutivo.

*Informe de verificación*

54. La verificación demostró que Santo Tomé y Príncipe cuenta con un sistema de otorgamiento de licencias eficaz y con una sólida dependencia nacional del ozono. Se han alcanzado los objetivos generales de consumo de SAO a nivel nacional para 2008 y 2009. El consumo real de SAO de 2008 fue de 0,2 toneladas PAO (en comparación con 0,7 toneladas PAO de consumo máximo permitido conforme al acuerdo) y nulo para 2009 (en comparación con 0,7 toneladas PAO de consumo máximo permitido conforme al acuerdo).

Observaciones de la Secretaría

55. El Gobierno de Santo Tomé y Príncipe ha notificado un consumo de CFC de 0,2 toneladas PAO con arreglo al Artículo 7 del Protocolo de Montreal en 2008 y un consumo nulo para 2009 y 2010. El sistema de otorgamiento de licencias y cuotas de Santo Tomé y Príncipe se aplica a las sustancias de los Anexos tanto A como C. Las cuotas anuales para estas sustancias son emitidas conjuntamente por los Ministerios de Medio Ambiente y de Comercio.

Recomendación de la Secretaría

56. El Comité Ejecutivo pudiera:

a) Tomar nota del informe de verificación del consumo de CFC para Santo Tomé y Príncipe para el período de 2007 a 2009 y del cumplimiento del país de sus obligaciones de eliminación respecto del consumo de CFC; y

b) Tomar nota además de que Santo Tomé a notificado un consumo nulo de CFC con arreglo al Artículo 7 del Protocolo de Montreal para 2009 y 2010.

## II. PLANES DE ELIMINACIÓN SECTORIALES

57. El PNUD y el Banco Mundial han presentado los siguientes informes:

a) China: eliminación de SAO en el sector de solventes de China (informe sobre la marcha de las actividades de 2010, verificación del desempeño de 2009 y 2010 y verificación técnica de 1,1,1-tricloroetano de 2010) (PNUD)

b) India: informe sobre la ejecución del plan de eliminación de CTC para los sectores de consumo y producción durante 2010 (Banco Mundial)

**China: eliminación de SAO en el sector de solventes de China (informe sobre la marcha de las actividades de 2010, verificación del desempeño de 2009 y 2010 y verificación técnica de 1,1,1-tricloroetano de 2010) (PNUD)**

58. En nombre del Gobierno de China, el PNUD como organismo de ejecución ha presentado los informes anuales sobre la marcha de las actividades de 2009 y 2010 para el plan para el sector de solventes para la eliminación de las SAO en China, así como la verificación del consumo de usos de 1,1,1-tricloroetano controlados para 2009 y 2010, y una verificación técnica de eliminación en una

muestra de tres empresas beneficiarias, para que sean considerados por el Comité Ejecutivo en su 66ª reunión.

*Antecedentes*

59. El plan para el sector de solventes de China fue aprobado en la 30ª reunión del Comité Ejecutivo, por un costo total de 52 millones $EUA más costos de apoyo para el PNUD. Los fondos se han aprobado en 11 tramos anuales para la ejecución desde 2000 hasta 2010, y el último tramo se aprobó en la 59ª reunión.

60. La eliminación se logró por medio de una combinación de actividades de inversión dirigidas a empresas específicas y un programa de asistencia técnica para empresas más pequeñas administrado mediante un sistema de comprobantes. Los límites de consumo se mantienen por medio de la regulación de la producción y la importación. La reducción de la producción se controla en el marco de los planes de eliminación para el sector de producción de CFC y CTC. El uso de CTC como solvente está prohibido desde el 1 de junio de 2003, y el uso de CFC-113 como solvente está prohibido desde el 1 de enero de 2006; por consiguiente, se han completado las actividades relacionadas en años anteriores. El uso de 1,1,1-tricloroetano como último solvente que contiene SAO y por cubrir en este plan en China debía eliminarse por completo antes del 1 de enero de 2010.

Eliminación a partir de proyectos y actividades de inversión

*Actividades en el nivel de las empresas*

61. Conforme al plan para el sector de solventes, las reducciones registradas en 2010 se lograron por medio de la terminación de las actividades de eliminación en las empresas en el marco del proyecto de contrato de reducción de SAO iniciado en 2008 y 2009 para eliminar los usos de 1,1,1-tricloroetano como solvente. En el año 2009 se ejecutaron actividades con una reducción total de 73,7 toneladas PAO de 1,1,1-tricloroetano, y de otras 3,7 toneladas PAO en el año 2010. En total, se logró la eliminación de 247,07 toneladas PAO de consumo de 1,1,1-tricloroetano en el plan para el sector de solventes durante un período de 11 años. En los años anteriores, las actividades para sustituir el CFC-113 habían dado lugar a una reducción acumulada de 2.689,5 toneladas PAO, mientras que las actividades relacionadas con el CTC habían logrado una reducción de 29,5 toneladas PAO. La eliminación se ha logrado por medio de 379 contratos separados. Las reducciones del consumo en los años 2009 y 2010, así como la eliminación planificada en el plan sectorial en comparación con las reducciones logradas, se muestran en el Cuadro 4 a continuación:

**Cuadro 4: Reducciones del consumo (2009 y 2010) y eliminación planificada en el plan para el sector de solventes de China**

<table>
<tr><th colspan="2">Sustancia en toneladas PAO</th><th>CFC-113</th><th>1,1,1-tricloroetano</th><th>CTC</th><th>Total</th></tr>
<tr><td colspan="2">2009</td><td>0</td><td>73,7</td><td>0</td><td>73,7</td></tr>
<tr><td colspan="2">2010</td><td>0</td><td>3,7</td><td>0</td><td>3,7</td></tr>
<tr><td rowspan="4">Acumulativo 2000-2010</td><td>Plan</td><td>3 300</td><td>537</td><td>110</td><td>3 947</td></tr>
<tr><td>Reducciones acumulativas en las empresas</td><td>2 689,5</td><td>247,1</td><td>29,5</td><td>2 966,1</td></tr>
<tr><td>Proporción (reducciones acumulativas en las empresas/plan)</td><td>81,5%</td><td>46,0%</td><td>26,8%</td><td>75,1%</td></tr>
<tr><td>Reducción real del consumo</td><td>3 300</td><td>537</td><td>110</td><td>3 947</td></tr>
</table>

62. El informe señala los motivos por los que la reducción real del consumo, es decir, la eliminación a nivel nacional, es diferente de las reducciones acumulativas de las empresas, que se abordaron en el plan de eliminación. Uno de los motivos es que varias empresas parecen haber eliminado el consumo de 1,1,1-tricloroetano por medio de actividades propias, sin financiación del proyecto. En segundo lugar, hay una gran cantidad de empresas que no resultan admisibles para la financiación, es decir, empresas con propiedad extranjera que consumen solventes con SAO, pero que no resultan admisibles para recibir financiación en este plan.

*Actividades de asistencia técnica*

63. En el marco del plan sectorial, se continuó con la ejecución de varias actividades de asistencia técnica que se habían iniciado en años anteriores. Esto incluyó actividades relacionadas con la lucha contra las importaciones, la producción y el uso ilícitos de SAO, tales como la terminación de un nuevo proyecto de “reglamento de gestión de la importación y exportación de SAO” en 2010, realización de talleres técnicos para funcionarios gubernamentales locales e investigación del consumo ilícito; y dos investigaciones concretas que analizaron el uso de CTC y CFC-113. También se continuó con la creación de capacidad para las oficinas de protección ambiental locales con el objetivo de permitir y fortalecer la supervisión del cumplimiento del Protocolo de Montreal. De las 18 provincias y ciudades objetivo de las actividades del plan para el sector de solventes, se recibieron informes de 12 ciudades en 2009. En el marco de la actividad de creación de capacidad para combatir el comercio ilícito de SAO, se imprimieron materiales de capacitación y materiales de información para las aduanas. Finalmente, se ha llevado a cabo una compleja verificación técnica, que se ha presentado a esta reunión.

64. También se han realizado varias actividades de aumento de la sensibilización y capacitación en el contexto del plan para el sector de solventes. Esto incluye actividades relacionadas con el sector de solventes el Día del Ozono, capacitación en políticas para autoridades locales en China, creación de capacidad para capacitación y comunicación para que las administraciones locales cumplan el Protocolo de Montreal, y apoyo relacionado para equipos de redes e instalaciones de conferencias. Finalmente, se han formulado diversas políticas y reglamentos; entre ellos, una prohibición nacional del uso de 1,1,1-tricloroetano para el 1 de enero de 2010 (que, por ende, el eliminaría el consumo) y del uso de 1,1,1-tricloroetano para las empresas para el 1 de enero de 2011.

65. La verificación de las actividades demostró que las actividades relacionadas se habían llevado a cabo. La verificación del consumo confirmó que el uso de CTC, 1,1,1-tricloroetano y CFC-113 en el sector de solventes había sido nulo en 2009 y 2010. La financiación restante se ha agotado completamente durante el año 2010, a partir de un nivel de 6.824.620 $EUA a fines de 2009, por lo que no restan saldos en la cuenta del proyecto.

Observaciones de la Secretaría

66. En noviembre de 2009, la 59ª reunión había aprobado varias actividades que debían llevarse a cabo con los fondos restantes para ese entonces, de más de 7 millones de $EUA. En 2010 el PNUD, en nombre del Gobierno de China, ejecutó dichas actividades y comprometió los fondos de proyecto restantes.

67. La información presentada por el PNUD en nombre de China proporcionó un excelente resumen general, muy detallado, de las actividades de este plan y de los resultados logrados tanto para 2009 y 2010 como desde el inicio del plan. Las verificaciones presentadas para 2009 y 2010 resultan suficientes para confiar plenamente en la exactitud de la información proporcionada. La ejecución del plan para el sector de solventes se ha completado.

Recomendación de la Secretaría

68. El Comité Ejecutivo pudiera:

a) Tomar nota del informe sobre la marcha de las actividades para 2009/2010 del plan para el sector de solventes para eliminar las SAO en China; y

b) Tomar nota de los informes relacionados de verificación de 1,1,1-tricloroetano para 2009 y 2010.

**India: informe sobre la ejecución del plan de eliminación de CTC para los sectores de consumo y producción durante 2010 (Banco Mundial)**

69. El Banco Mundial había presentado a la 65ª reunión, en calidad de organismo de ejecución principal y en nombre del Gobierno de la India, la verificación de los logros del programa anual para 2010. En el contexto de esta presentación, el Comité Ejecutivo había tomado nota, en su decisión 65/10 j), de que en el informe de verificación se recoge que el uso de CTC para la producción de monómero de cloruro de vinilo (VCM) se había clasificado como uso de materia prima desde principios del año 2005, mientras que en 2007 la 19ª Reunión de las Partes en el Protocolo de Montreal ya había clasificado el uso de CTC en la producción de dicho monómero como aplicación de agentes de procesos (decisión XIX/15). El Comité Ejecutivo también había pedido al Banco Mundial en el inciso iii) de la decisión que solicitara a la India que actualizara consecuentemente los datos del consumo de CTC para el período desde 2008 hasta 2010 notificados a la Secretaría del Ozono en virtud del Artículo 7 del Protocolo de Montreal. En el inciso iv) de la misma decisión, pidió al Banco Mundial que se coordinase con el Gobierno de la India para investigar hasta qué punto los volúmenes de CTC destruidos durante los años 2008, 2009 y 2010 compensarían los de CTC utilizados como agente de procesos en la producción de monómero de cloruro de vinilo durante estos mismos años, y que facilitara un informe a más tardar ocho semanas antes de la 66ª reunión.

70. Con posterioridad a la 65ª reunión, la 23ª Reunión de las Partes deliberó acerca de la cuestión del CTC para usos como agente de procesos en general y del monómero de cloruro de vinilo en particular. En el párrafo 8) de la decisión XXIII/7, “Uso de sustancias controladas como agentes de procesos”, estipula que las Partes consideran “el uso del tetracloruro de carbono para la producción de monómero de cloruro de vinilo, a los fines de los niveles calculados de consumo y producción, de modo excepcional, como un uso como materia prima hasta el 31 de diciembre de 2012”. En virtud de la decisión antes mencionada, los incisos iii) y iv) de la decisión 65/10 j) del Comité Ejecutivo quedan obsoletos.

71. En la decisión 65/10 j) v) se pidió al Banco Mundial que proporcionara un informe sobre la ejecución del plan de eliminación de CTC para los sectores de consumo y producción durante el año 2010, a tiempo para la 66ª reunión y, si correspondiese, una revisión de las actividades planificadas. El informe presentado por el Banco Mundial indicaba que las auditorías de verificación técnica de la producción y el consumo de CTC para 2010 se llevaron a cabo en marzo de 2011. El Banco contrató a un equipo de auditoría independiente para realizar visitas a los sitios y examinar la documentación en cuatro productores de CTC, ocho productores de cloruro de ácido de dicloro vinil (DVAC), un productor de monómero de cloruro de vinilo y una planta de benzofenona de difluor (DBBP) y en las tres plantas de almacenamiento del puerto de Kandla. Para 2010, la Célula del Ozono no emitió ninguna cuota para venta a usuarios para usos diferentes de materia prima. El equipo de auditoría confirmó que no hubo ventas directas a usuarios diferentes de usuarios de materia prima y que los productores de CTC no importaron ni exportaron CTC. El equipo de auditoría independiente verificó, por lo tanto que, en su opinión, la India se encontraba en situación de cumplimiento de sus obligaciones conforme al Protocolo de Montreal. El último desembolso, también final, de fondos del plan de eliminación de CTC (2,1 millones de $EUA) a

los cuatro productores de CTC se realizó en diciembre de 2010. En 2011, la Célula Nacional del Ozono llevó a cabo varios talleres y actividades de capacitación en el marco del componente de asistencia técnica.

72. El Banco Mundial informó a la Secretaría que los fondos restantes ascienden a 1,4 millones de $EUA, destinados a cubrir: capacitación de agrupamientos y asociaciones de la industria que utilizan CTC para trabajar con solventes de alternativa (400.000 $EUA); desarrollo y aplicación de una estrategia de comunicación para evitar el uso de CTC y evitar el retorno al uso por parte de los usuarios (290.000 $EUA); capacitación de funcionarios del gobierno y de juntas de control de contaminación (196.000 $EUA); talleres de capacitación para funcionarios de aduanas (196.000 $EUA); producción de una publicación con relatos de éxitos (38.000 $EUA); y actividades continuas de la unidad de gestión de proyecto, incluida supervisión (280.000 $EUA). La Secretaría señaló el hecho de que el CTC para usos controlados ya se ha eliminado desde hacía más de un año. Planteó una grave preocupación acerca de la posible doble financiación en comparación con actividades anteriores del plan sectorial así como con la capacitación aduanera solicitada originalmente en el marco del plan de gestión de eliminación de los HCFC presentado para la India en la 66ª reunión. La Secretaría también planteó cuestiones relacionadas con el monto de financiación previsto para las diferentes actividades y formuló diversas sugerencias, tales como añadir actividades para supervisar el CTC para usos no controlados que se desvía a usos controlados y transferencia de fondos a otras actividades como el plan de gestión de eliminación de los HCFC.

73. El Banco Mundial, en nombre del Gobierno de la India, decidió retirar la presentación considerando que el estudio de diferentes posibilidades para asignar la financiación requeriría más tiempo. No obstante, la Secretaría consideró que era necesario presentarla al Comité Ejecutivo en vista de la decisión XXIII/7 de la Reunión de las Partes y de la decisión 65/10 j) v), que pedía que se presentara un informe a la 66ª reunión.

74. El Comité Ejecutivo pudiera considerar:

a) Señalar que el párrafo 8 de la decisión XXIII/7 de la 23ª Reunión de las Partes que considera el uso del tetracloruro de carbono para la producción de monómero de cloruro de vinilo, a los fines de los niveles calculados de consumo y producción, de modo excepcional, como un uso como materia prima hasta el 31 de diciembre de 2012, sustituye los incisos iii) y iv) de la decisión 65/10 j) del Comité Ejecutivo;

b) Pedir al Banco Mundial que proporcione a la 69ª reunión un informe sobre la situación del uso de tetracloruro de carbono para la producción de monómero de cloruro de vinilo en la India;

c) Tomar nota del informe sobre la ejecución del plan de eliminación de CTC para los sectores de consumo y producción de la India en 2010 y de la verificación relacionada presentada; y

d) Pedir al Banco Mundial que presente a la 67ª reunión un plan de trabajo que cubra los fondos restantes del plan de eliminación de CTC en la India.

## III. FORTALECIMIENTO INSTITUCIONAL

**Informe sobre la marcha de las actividades de la aplicación de la decisión 64/20 sobre el proyecto de fortalecimiento institucional para la República Popular Democrática de Corea (PNUMA)**

*Antecedentes*

75. En la 64º reunión, el Comité Ejecutivo decidió aplazar la consideración de la solicitud para la etapa VI del proyecto de fortalecimiento institucional para la República Popular Democrática de Corea hasta la 66ª reunión, y pidió a la Secretaría y al PNUMA como organismo de ejecución que propusieran al Comité Ejecutivo métodos de desembolso, estructuras organizacionales y procedimientos de supervisión alternativos antes de la 66ª reunión (decisión 64/20). El PNUMA ha presentado un informe sobre la aplicación de la decisión 64/20 (Apéndice I).

*Propuesta de métodos de desembolso, estructuras organizacionales y procedimientos de supervisión alternativos*

76. El informe describe la modalidad actual para el desembolso de fondos para el proyecto de fortalecimiento institucional y el proceso de consulta que se llevó a cabo entre el PNUMA, el Comité nacional de coordinación para el medio ambiente (NCCE)/dependencia nacional del ozono de la República Popular Democrática de Corea y el PNUD (Pyongyang) entre el 28 de noviembre y el 1 de diciembre de 2011. También se llevaron a cabo deliberaciones entre la Oficina regional para Asia y el Pacífico (ROAP) del PNUMA y la Comisión Económica y Social para Asia y el Pacífico (CESPAP).

77. Sobre la base de los resultados de estas deliberaciones, se presenta una propuesta en el informe adjunto (Apéndice I); esta puede sintetizarse como sigue:

<u>Desembolso</u>

- El PNUMA y el NCCE firman un acuerdo financiero para definir con claridad todas las actividades de fortalecimiento institucional y los costos respectivos.
- Según un plan de trabajo anual detallado, el PNUMA hace pagos adelantados en won coreanos a la dependencia nacional del ozono a través de la oficina del PNUD en Pyongyang.
- Con una antelación de por lo menos un mes a una actividad propuesta, la dependencia nacional del ozono presentaría un mandato detallado para que sea avalado por el PNUMA, lo que permitiría usar los fondos adelantados para esa actividad.
- Dos semanas después de haberse completado la actividad, la dependencia nacional del ozono presentaría un informe detallado de la actividad realizada en comparación con el mandato avalado, incluyendo informes de gastos y recibos originales para que sean examinados y supervisados por el PNUMA.
- Los pagos adelantados de fondos de fortalecimiento institucional no podrían cubrir ninguna actividad organizada sin el aval previo del PNUMA.

<u>Estructuras organizacionales y procedimientos de supervisión</u>

- El personal de la dependencia nacional del ozono continuaría siendo contratado por el gobierno y situado en el Ministerio de Ambiente y Protección de la Tierra.

Procedimientos de supervisión

- Informe sobre la marcha de las actividades semestral conforme a lo requeridos por los procedimientos del PNUMA para todos los países.
- Mandato con aval previo para las actividades.
- Informe sobre las actividades dentro de las dos semanas posteriores a la terminación.
- Cuando fuera posible, participación del personal del PNUMA en las actividades de fortalecimiento institucional.
- El Programa de asistencia al cumplimiento del PNUMA intentaría organizar visitas semestrales de examen y supervisión (el NCCE convino en brindar acceso sin restricciones a los sitios de los proyectos).

Recomendación de la Secretaría

78. El Comité Ejecutivo pudiera:

a) Tomar nota del informe presentado por el PNUMA acerca de la aplicación de la decisión 64/20 del Comité Ejecutivo acerca del proyecto de fortalecimiento institucional para la República Popular Democrática de Corea; y

b) Considerar si los métodos de desembolso, estructuras organizacionales y procedimientos de supervisión alternativos responden a las preocupaciones manifestadas por el Comité Ejecutivo en su 64ª reunión.

## IV. MOVILIZACIÓN DE RECURSOS PARA LOGRAR COBENEFICIOS CLIMÁTICOS

79. En la 63ª reunión, el Comité Ejecutivo aprobó fondos por valor de 680.000 $EUA para cuatro proyectos mundiales de movilización de recursos individuales que serían ejecutados por el PNUD (200.000 $EUA), el PNUMA (100.000 $EUA), la ONUDI (200.000 $EUA) y el Banco Mundial (180.000 $EUA). Estos proyectos tienen el objetivo de movilizar recursos para lograr beneficios climáticos más allá de aquellos que se lograrían con la eliminación de HCFC por sí sola. Los proyectos se aprobaron con la condición de que se presentaría un informe provisional a la 66ª reunión que incluiría diversos elementos específicos: adicionalidad de los proyectos propuestos; transparencia y gobernanza, además de tratar la liquidez; las garantías de que estos proyectos no se convertirían en incentivos perversos para los países; el examen de las posibilidades de compartir los beneficios, incluida la devolución de fondos al Fondo Multilateral; adopción de las medidas necesarias para asegurar la sostenibilidad de los proyectos propuestos; eliminación de duplicaciones con proyectos similares; información sobre los costos de las transacciones. Se pidió a los organismos que presenten un informe final sobre los proyectos a la 69ª reunión. Los fondos aprobados se tomaron del presupuesto reservado para proyectos sin especificar que se había establecido por separado con los fondos reembolsados del proyecto de enfriadores de Tailandia.

### Mundial: movilización de recursos para lograr cobeneficios climáticos (PNUD)

80. Se encomendó al PNUD la tarea de preparar cuatro proyectos de demostración piloto en el sector de fabricación de refrigeración y acondicionadores de aire para examinar la intervención técnica para mejorar la eficiencia energética y las medidas nacionales de políticas y reglamentos para sostener dicha intervención con miras a aumentar al máximo el efecto en el clima de la eliminación de los HCFC, que se financiarían como actividades de movilización de recursos. Se pidió al PNUD que informe al Comité Ejecutivo, en la 67ª reunión a más tardar, acerca de las cuatro propuestas anteriormente especificadas,

observándose que ello sería solamente a título informativo y que las propuestas no serían financiadas por el Fondo Multilateral.

*Progresos*

81. El PNUD ha procurado movilizar recursos de fuentes bilaterales y multilaterales así como del sector privado que se podrían aplicar en el nivel de las empresas, los subsectores y los sectores. Estados Unidos de América ha transferido al PNUD 1,7 millones de $EUA para demostración y aplicación de tecnología de bajo PCA y alta eficiencia energética en subsectores seleccionados de países de la región de Asia y el Pacífico. El PNUD ha proporcionado apoyo técnico para la preparación de una propuesta de proyecto del FMAM para Indonesia centrada en la financiación de mejoras de eficiencia energética en los sectores de aire acondicionado y refrigeración. La propuesta, por valor de 4,5 millones de $EUA, está siendo finalizada para su presentación y proporcionará oportunidades para reproducirla en otros países. El PNUD continúa trabajando con otros donantes bilaterales para movilizar fondos para mejoras de eficiencia energética y alternativas con bajo potencial de calentamiento atmosférico (PCA). El organismo también se ha comunicado con proveedores de tecnología del sector privado (sectores de espumas, aire acondicionado y refrigeración) para procurar inversiones adicionales en alternativas de bajo PCA y alta eficiencia energética a través de subsidiarias en los países que operan al amparo del Artículo 5.

<u>Recomendación de la Secretaría</u>

82. El Comité Ejecutivo pudiera tomar nota del informe provisional sobre movilización de recursos para obtener cobeneficios climáticos presentado por el PNUD y reiterar su decisión 63/20 a) i), en la que se pidió al PNUD que informara al Comité Ejecutivo acerca de las cuatro propuestas especificadas anteriormente a más tardar en la 67ª reunión, observando que ello sería solamente a título informativo y que dichas propuestas no recibirían financiación del Fondo Multilateral.

**Mundial: movilización de recursos en cooperación con otros organismos para lograr cobeneficios climáticos por la eliminación de los HCFC en los países de bajo consumo en los que solo hay sector de servicio y mantenimiento (PNUMA)**

83. El Comité Ejecutivo aprobó la financiación para un estudio sobre opciones de financiación, talleres regionales sobre cofinanciación, y/o una o más de las aplicaciones piloto de cofinanciación para uno o más países de bajo consumo que tengan ya aprobado un plan de gestión de eliminación de HCFC. Se pidió al PNUMA que se asegurara de que los talleres regionales se celebrasen en el contexto de las reuniones de red en el marco del Programa de Asistencia a la Cumplimiento del PNUMA a fin de asegurar la rentabilidad, y de que las fechas de la celebración de tales talleres permitiesen incorporar las experiencias de otros organismos en sus actividades de movilización de recursos.

*Progresos*

84. Se ha redactado el mandato para el estudio sobre opciones de financiación y se ha compilado una lista de los posibles consultores expertos que realizarían el estudio. Se ha preparado una lista inicial de posibles invitados para el taller regional, y los equipos del Programa de asistencia al cumplimiento están planificando los talleres regionales en el contexto de las reuniones de redes y temáticas previstas para 2012. Los aspectos relacionados con la cofinanciación se abordarán durante el taller temático para los países de lengua francesa del África septentrional y occidental que se realizará en Burkina Faso en abril de 2012, y el PNUMA está considerando si se aplicaría un proyecto de movilización de recursos para países de bajo volumen de consumo a ese taller.

Recomendación de la Secretaría

85. El Comité Ejecutivo pudiera tomar nota del informe provisional sobre el proyecto para movilización de recursos para lograr cobeneficios climáticos por la eliminación de los HCFC en los países de bajo consumo en los que solo hay sector de servicio y mantenimiento en cooperación con otros organismos, presentado por el PNUMA.

**Mundial: movilización de recursos para la eliminación de los HCFC y cobeneficios climáticos (ONUDI)**

86. El Comité Ejecutivo aprobó fondos para la preparación de dos propuestas de proyecto sobre una posible cofinanciación para actividades relacionadas con los HCFC con la condición de que la ONUDI informara al Comité Ejecutivo acerca de las dos propuestas especificadas anteriormente en la 67ª reunión a más tardar, observándose que ello sería solamente a título informativo y que las propuestas no serían financiadas por el Fondo Multilateral.

*Progresos*

87. La ONUDI ha identificado posibles países de África, América Latina y Asia y el Pacífico para dos conversiones piloto en los sectores de pesca y procesamiento de alimentos. La ejecución de los proyectos se llevará a cabo en cuatro etapas: adopción y adaptación de los enfoques disponibles para apoyar los costos no admisibles relacionados con la eliminación de los HCFC; identificación y aplicación de la tecnología de alternativa más prometedora para sustituir las instalaciones existentes y ejecución de la conversión o las conversiones piloto; supervisión del rendimiento de la tecnología convertida y evaluación de los ahorros de energía; y diseño del plan financiero más prometedor para apalancar fondos adicionales para la conversión de instalaciones similares.

Recomendación de la Secretaría

88. El Comité Ejecutivo pudiera tomar nota del informe provisional sobre el proyecto para movilización de recursos para eliminar los HCFC y obtener cobeneficios climáticos presentado por la ONUDI y reiterar su decisión 63/23 a) i), en la que se pidió a la ONUDI que informara al Comité Ejecutivo acerca de las dos propuestas especificadas anteriormente a más tardar en la 67ª reunión, observando que ello sería solamente a título informativo y que dichas propuestas no recibirían financiación del Fondo Multilateral.

**Mundial: movilización de recursos para estudiar los beneficios colaterales de la eliminación de los HCFC (Banco Mundial)**

89. El Comité Ejecutivo aprobó fondos para un estudio que se centraría únicamente en la monetización de los derechos de emisión de carbono.

*Progresos*

90. El Banco Mundial preparó una nota de concepto revisada centrada en el proyecto sobre uso de mecanismos del mercado en el nivel de los proyectos, tomando en cuenta los resultados relacionados con las finanzas del carbono logrados en la Conferencia sobre Cambio Climático de las Naciones Unidas llevada a cabo en Durban en 2011. El estudio será llevado a cabo por una firma consultora con la supervisión del Banco Mundial, y se completará antes del 31 de diciembre de 2012, con miras a presentar el informe final a la 69ª reunión, conforme a la decisión 63/24.

Recomendación de la Secretaría

91. El Comité Ejecutivo pudiera tomar nota del informe provisional sobre movilización de recursos para un estudio de beneficios colaterales de la eliminación de los HCFC presentado por el Banco Mundial.

## V. PROYECTOS DE DESTRUCCIÓN DE SAO

92. En las decisiones 58/19 a) iii) y 64/50, se reiteró que los organismos bilaterales y de ejecución debían informar anualmente a la primera reunión del Comité Ejecutivo sobre los progresos y las experiencias adquiridas en los proyectos de demostración sobre destrucción de SAO, a partir del primer año después de la aprobación de los proyectos, e incluir en dichos informes datos sobre: las cantidades de las diferentes SAO acopiadas o identificadas, transportadas, almacenadas y destruidas, así como sobre arreglos financieros, administrativos y de cofinanciación y cualquier otra cuestión pertinente. Conforme a dichas decisiones, se presentaron a la 66ª reunión informes sobre los proyectos de destrucción de SAO en curso en Cuba y Ghana.

### Cuba: informe de situación sobre el proyecto piloto de demostración de gestión y destrucción de desechos de SAO (PNUD)

*Antecedentes*

93. El proyecto piloto de demostración de gestión y destrucción de desechos de SAO en Cuba fue aprobado en la 62ª reunión por un monto de 525.200 $EUA para destruir en total 45,3 toneladas métricas de desechos de SAO, en la inteligencia de que no se proporcionaría a Cuba financiación para ningún otro proyecto de destrucción de SAO en el futuro (decisión 62/27). La finalidad del proyecto piloto es desarrollar un marco de logística eficiente y rentable para el transporte, el almacenamiento y la destrucción de las SAO en Cuba.

*Progresos*

94. El documento de proyecto del PNUD y Cuba se firmó en junio de 2011, y se ha establecido un equipo de proyecto con la plena participación de todos los interesados. Entre los progresos logrados se incluyen: especificaciones técnicas e identificación de los equipos necesarios para adaptar las instalaciones elegidas para la destrucción de SAO (la construcción y montaje de las instalaciones comenzará en 2012); identificación de los requisitos operacionales y equipos para las instalaciones de almacenamiento provinciales; el diseño de un camión especializado para acopio y transporte de SAO; y revisión del marco jurídico para asegurar que se reglamente la destrucción de las SAO.

95. Todavía no se han iniciado las tareas de acopio y destrucción en sí; no obstante, los ensayos comenzarán una vez que se haya completado la instalación inicial.

Observaciones de la Secretaría

96. A diciembre de 2011, no se habían desembolsado fondos, dado que las actividades iniciales para los ajustes en la construcción de las instalaciones son cofinanciados por el Gobierno de Cuba.

97. Actualmente, hay 130 tm de reservas de SAO almacenadas en un almacén regional. El PNUD indicó que todas las reservas son desechos de SAO y que no pueden ser recicladas o regeneradas.

Recomendación de la Secretaría

98. El Comité Ejecutivo pudiera:

a) Tomar nota del informe de situación sobre el proyecto piloto de demostración de gestión y destrucción de desechos de SAO para Cuba presentado por el PNUD; y

b) Pedir al PNUD que presente a la 69ª reunión del Comité Ejecutivo un informe sobre los progresos logrados y la experiencia adquirida en el proyecto piloto de demostración para Cuba conforme a las decisiones 58/19 a) iii) y 64/50.

**Ghana: informe de situación sobre el proyecto piloto de demostración de gestión y destrucción de desechos de SAO (PNUD)**

*Antecedentes*

99. El proyecto piloto de demostración de gestión y destrucción de desechos de SAO en Ghana fue aprobado en la 63ª reunión, por un monto de 198.000 $EUA para destruir en total 8,8 toneladas métricas de desechos de SAO. El proyecto está integrado en el plan de gestión de eliminación de los HCFC del país y en el proyecto de eficiencia energética (EE) del Fondo para el Medio Ambiente Mundial, mediante el cual se recogerán y desmantelarán refrigeradores al fin de su vida útil e ineficientes en cuanto al uso de energía retirados en forma anticipada en almacenes regionales a fin de recuperar las SAO. El 9 de mayo de 2011 se recibió la confirmación de la financiación (1.722.727 $EUA) para el proyecto de EE del FMAM, lo que permitió desembolsar los fondos para el proyecto piloto (decisión 63/27).

*Progresos*

100. Un consultor internacional contratado en el marco del proyecto asistió al taller de introducción del proyecto de EE del FMAM que se llevó a cabo en Accra los días 15 y 16 de noviembre de 2011. El taller contó con la asistencia de interesados clave de los sectores público y privado y brindó al consultor oportunidad de deliberar acerca de cuestiones relacionadas con: centros de desmantelamiento y recuperación regionales descentralizados; mantenimiento de registros de refrigeradores retirados; procesos seguros para el desmantelamiento de refrigeradores retirados; recuperación, almacenamiento y transporte de SAO; prueba de la composición de las SAO; procesos de exportación; registros y cadena de custodia; capacitación de técnicos. Se consideró esencial establecer una estrecha coordinación entre el proyecto de destrucción, el plan de gestión de eliminación de los HCFC y el proyecto del FMAM para asegurar un flujo estable de acopio y destrucción de SAO.

101. La unidad del Protocolo de Montreal del PNUD tiene previsto visitar Accra en abril de 2012 para deliberar acerca de la logística del Centro de destrucción de SAO y otras actividades del proyecto.

Observaciones de la Secretaría

102. De los 198.000 $EUA aprobados para el proyecto, se han desembolsado 21.000 $EUA para contratos de consultoría nacional e internacional. El PNUD informó a la Secretaría que no había aún información acerca de los tipos de SAO que se procesarían, dado que el proyecto acaba de iniciarse; no obstante, la gran mayoría de las SAO almacenadas en el organismo de protección ambiental de Ghana y el flujo de SAO que se espera del proyecto de EE del FMAM son CFC, que fueron identificados como desechos disponibles para destrucción cuando se aprobó el proyecto.

103. El PNUD notificó a la Secretaría que el proyecto ha comenzado con cierta lentitud dado que era importante que la visita a Ghana del consultor internacional en 2011 coincidiera con el taller de introducción del proyecto de EE del FMAM, a fin de asegurar que se hubieran establecido modalidades para sinergias entre ambos proyectos. Este se había demorado debido a la tardanza en la firma del documento del proyecto de EE del FMAM.

Recomendación de la Secretaría

104. El Comité Ejecutivo pudiera:

a) Tomar nota del informe de situación sobre el proyecto piloto de demostración de gestión y destrucción de desechos de SAO para Ghana presentado por el PNUD; y

b) Pedir al PNUD que presente a la 69ª reunión del Comité Ejecutivo un informe sobre los progresos logrados y la experiencia adquirida en el proyecto piloto de demostración para Ghana conforme a las decisiones 58/19 a) iii) y 64/50.

## VI. PROYECTOS DE DEMOSTRACIÓN E INVERSIÓN RELACIONADOS CON HCFC

105. El PNUD presentó dos informes sobre la marcha de las actividades detallados sobre los siguientes proyectos para HCFC:

a) Mundial: informe sobre la evaluación del metilal como agente espumante en la fabricación de sistemas de espumas de poliuretano (PNUD)

b) Mundial: informe sobre la evaluación de opciones de bajo costo para el uso de hidrocarburos en la fabricación de espumas de poliestireno (PNUD)

**Mundial: Metilal como agente espumante en la fabricación de sistemas de espumas de poliuretano. Una evaluación para la aplicación en proyectos del Fondo Multilateral**

*Antecedentes*

106. El PNUD ha presentado a la 66ª reunión un informe técnico sobre el metilal como agente espumante en la fabricación de sistemas de espumas de poliuretano: una evaluación para la aplicación en proyectos del Fondo Multilateral. El informe técnico completo se adjunta a este documento (Apéndice II).

107. En la 58ª reunión, el Comité Ejecutivo aprobó un proyecto piloto para la validación del metilal como agente espumante en la fabricación de espumas de poliuretano, dando por entendido que el equipo de laboratorio necesario para la validación de la tecnología sería donado a una institución de investigación sin fines comerciales una vez terminadas las fases I y II del proyecto de demostración (decisión 58/30).

*Resumen ejecutivo*

108. El PNUD preparó diversos proyectos piloto para investigar el uso seguro del metilal como sustancia sustitutiva del HCFC-141b en aplicaciones de espumas de poliuretano. El uso de sistemas a base de metilal ha sido evaluado en Arinos Quimca, Ltd. (Brasil), con el objetivo de evaluar su rendimiento en comparación con los sistemas a base de HCFC-141b a fin de determinar si la tecnología resulta viable para el uso en proyectos del Fondo Multilateral.

109. A fin de asegurar que la tecnología de metilal estaría disponible en todo el mundo, el PNUD evaluó la situación de la oferta. Proveen metilal fabricantes de Bélgica, China, la India, la República de Corea y el Reino Unido de Gran Bretaña e Irlanda del Norte. Si bien se ha patentado el metilal para varias aplicaciones en espumas de poliuretano, no se ha registrado ningún intento de obtención de licencias para su uso. Sobre la base de esta información, se cree que ninguna de esas patentes puede reclamar derechos efectivos y plenos sobre el uso del metilal en espumas de poliuretano. Por lo tanto, puede inferirse que el metilal está comúnmente disponible y es de uso libre en aplicaciones de espumas.

110. La evaluación del metilal en aplicaciones de espumas de poliuretano abordó lo siguiente: consideraciones relativas a salud, seguridad y medio ambiente; cuestiones relativas a su procesabilidad (p. ej., estabilidad, compatibilidad, transporte y almacenamiento); composición del sistema; una breve descripción de las propiedades físicas obtenidas en ensayos para diferentes aplicaciones; y costos indicativos de la conversión para la introducción de la tecnología en proveedores de sistemas y empresas de espumas.

111. Se evaluaron 16 aplicaciones de espumas de poliuretano que utilizan HCFC-141b como agente espumante para estudiar sus posibilidades de conversión al uso de metilal. Para la evaluación, se llevaron a cabo las siguientes actividades: adquisición de los equipos de prueba/prototipos necesarios; optimización y validación de 16 fórmulas en equipos de prototipos; desarrollo de prácticas seguras para cumplir las normas nacionales e internacionales de transporte, almacenamiento y uso de metilal en proveedores de sistemas y de sistemas que contienen metilal en empresas pequeñas y medianas (EPM); y difusión de la experiencia adquirida por medio de un taller. En el cuadro 5 a continuación se presenta una descripción general resumida de la evaluación.

**Cuadro 5: Evaluación de aplicaciones de espumas para la conversión a metilal**

| Aplicación | Salud, seguridad, medio ambiente | Procesabilidad | Propiedades físicas | Evaluación |
|---|---|---|---|---|
| **Espumas no destinadas a aislamiento** | | | | |
| Flexibles | + | + | + | + |
| Suelas de zapatos | + | + | + | + |
| Estructurales (rígida) | + | + | + | + |
| Semiflexibles | + | + | + | + |
| Moldeadas flexibles | + | + | + | + |
| Bloques de espumas hipersuaves | + | + | + | + |
| Moldeadas viscoelásticas | + | + | + | + |
| Bloques viscoelásticos | + | + | + | + |
| Espumas para embalajes | + | + | + | + |
| **Espumas para aislamiento** | | | | |
| Refrigeración | + | + | + | +/- |
| Calentadores de agua | + | + | + | +/- |
| Camiones | + | + | + | +/- |
| Bloques, paneles | + | + | + | +/- |
| Pulverizada | + | + | + | +/- |
| Thermoware | + | + | + | +/- |
| Espuma de poliisocianurato (PIR) | + | + | + | +/- |

+ Buena, - Deficiente; +/- Regular (aceptable con condiciones)

112. Conforme a la evaluación, el uso de metilal como agente espumante de alternativa para sustituir el HCFC-141b en aplicaciones de espumas de poliuretano puede ser viable. Los resultados indicaron que el metilal se adecua mejor a las espumas no destinadas a aislamiento que a las espumas para aislamiento. Tomando en cuenta que la comparación se hace entre sistemas a base de HCFC-141b optimizados y sistemas basados en metilal recientemente desarrollados, los resultados para las espumas rígidas (para aislamiento) ocasionaron una penalidad en el valor de aislamiento de hasta el 10%. Por lo tanto, las empresas deberían evaluar en forma individual el uso y una mayor optimización de los sistemas de metilal. Además, la adopción de la tecnología de metilal debería estar sujeta a las siguientes condiciones: la conversión de las empresas debería realizarse preferentemente a través de proveedores de sistemas locales; durante la preparación del proyecto, se debe verificar la compatibilidad de la sustancia química; y se deben tomar en cuenta las consideraciones relativas a la inflamabilidad de la sustancia.

113. El PNUD ha preparado plantillas generales de costos para calcular el costo adicional de la conversión de espumas a base de HCFC-141b a espumas a base de metilal. Los costos de capital (que se muestran en el cuadro 6 a continuación) y el costo de la sustancia química pueden variar en gran medida en diferentes países y también están sujetos a consideraciones relativas a economías de escala.

**Cuadro 6: Costos de capital relacionados con la conversión de espumas a base de HCFC-141b a espumas a base de metilal**

| Descripción | Costo indicativo ($EUA) | Observación |
|---|---|---|
| **Proveedores de sistemas** | | |
| Protección a prueba de explosiones en tanques de mezcla | AA x 30 000 | Igual que para el formiato de metilo |
| Distribuidor de nitrógeno | BB x 8 000 | |
| Monitores de vapores de metilal | 2 x 2 500 | Para controlar el cumplimiento de normas de higiene industrial |
| Paquete de seguridad de pulverizador/tubería compuesta (PIP) | CC x 7 500 | Escape, conexión a tierra |
| Paquete de seguridad para distribuidor de baja/alta presión | DD x 15 000 | Escape, conexión a tierra |
| Picnómetro (probador de celda cerrada) | 10 000 | |
| Probador de factor K portátil | 10 000 | |
| Refractómetro (prueba de pureza química) | 10 000 | |
| Distribuidor pequeño para alquiler | EE x 15 000 | |
| Gestión de proyecto | FF clientes a 1 000 | |
| Supervisión y transferencia de tecnología | 30 000 | |
| Gastos imprevistos | 10% de los costos de capital | |
| **Cliente (empresas de espumas)** | | |
| Monitor de vapores de metilal | FF x 2 500 | Para supervisar el cumplimiento de normas de higiene industrial* |
| Paquetes de retroadaptación de pulverizador/tubería compuesta | GG x 7 500 | Escape, conexión a tierra |
| Paquete de retroadaptación para distribuidor de baja/alta presión | HH x 15 000 | Escape, conexión a tierra |
| Distribuidores nuevos | II x 25 000 | Incluir paquetes de seguridad |
| Ensayos, pruebas capacitación | KK máquinas a 3 000 | Como en los proyectos aprobados |
| Gastos imprevistos | 10% de los costos de capital | |

*Conclusión del revisor técnico*

114. El revisor técnico llegó a la conclusión de que el uso de metilal como sustancia de alternativa para los sistemas a base de HCFC-141b en la fabricación de espumas de poliuretano en los países que operan al amparo del Artículo 5 parece ser una solución viable que cumple con los objetivos de una tecnología sustitutiva rentable, de valor de PAO nulo y PCA bajo. Las propiedades finales de la espuma son comparables a las de las espumas a base de HCFC-141b. El revisor técnico recomendó además que el informe, entre otras cosas, debería: definir los parámetros de los resultados de las pruebas para proporcionar orientación acerca de si las condiciones de funcionamiento reales pueden predecir los resultados en cuanto a la densidad de las espumas; proporcionar un cálculo estimado de los costos adicionales de explotación basado en los resultados obtenidos; continuar los estudios de estabilidad a largo plazo de las propiedades de las espumas, especialmente de la estabilidad de las dimensiones; incluir los equipos de supervisión como un componente integral de cada proyecto para garantizar la seguridad del funcionamiento y del personal.

Observaciones de la Secretaría

115. El proyecto piloto para la evaluación del metilal incluyó un taller para divulgar los resultados del proyecto que se realizó en el Brasil en diciembre de 2011. Asistieron más de 100 representantes, entre los que se incluyeron representantes de: 12 proveedores de sistemas del Brasil (ocho de propiedad local, a saber Amino, Arinos, Ariston, M.Cassab, Polisystem, Polyurethane, Purcom y Utech, y cuatro de propiedad extranjera, a saber Bayer, BASF, Dow y Huntsman); 13 empresas fabricantes de espumas del Brasil, Jamaica y Trinidad y Tabago; cinco países que operan al amparo del Artículo 5 (a saber, Colombia, Panamá, Paraguay, Perú y Jamaica); el PNUD, el PNUMA y Alemania; tres asociaciones de la industria del Brasil; ocho fabricantes/distribuidores de agentes espumantes del Brasil, Bélgica y los Estados Unidos de América; seis fabricantes de equipos de inyección de espumas; y cuatro miembros del Comité de opciones técnicas de espumas (FTOC).

116. En respuesta a un pedido de aclaraciones acerca de las retroadaptaciones de equipos y/o los equipos nuevos que se requerirían para introducir la tecnología de metilal, el PNUD explicó que dicha tecnología generalmente puede implementarse sin cambiar los equipos de base. Los costos reales se relacionan principalmente con la conexión a tierra del distribuidor de espuma, la instalación de un sensor de metilal (o, como alternativa, estudios de higiene industrial regulares a cargo de los proveedores de sistemas) y escapes de emisiones. Solo se requieren equipos nuevos en aquellos casos en que el usuario realiza la espumación en forma manual.

117. Al responder una pregunta acerca de si hay patentes y/o derechos de propiedad intelectual que cubran el uso de metilal como agente espumante, el PNUD indicó que hay varias patentes para algunas aplicaciones del metilal. Sin embargo, no hay ninguna patente que cubra de manera general el uso del metilal como agente espumante en espumas de poliuretano, y ninguna entidad empresarial o de otra índole ha intentado reclamar la propiedad de la tecnología para la aplicación en estudio. Dado que el metilal ha sido utilizado (y continúa siendo utilizado) por varios grandes fabricantes de productos químicos en aplicaciones de poliuretano y además por alrededor de 30 empresas en Europa, resultaría muy difícil que alguien pudiera reclamar esta tecnología y aplicar licencias. Por lo tanto, Lambiotte, Arinos y UNDP son de la opinión de que la tecnología es de uso libre.

118. Tras abordar todas las observaciones planteadas por la Secretaría y por el revisor técnico, el PNUD modificó del modo consiguiente el informe del proyecto de demostración.

Recomendación de la Secretaría

119. El Comité Ejecutivo pudiera:

a) Tomar nota con agradecimiento del informe titulado “Metilal como agente espumante en la fabricación de sistemas de espumas de poliuretano. Una evaluación para la aplicación en proyectos del Fondo Multilateral”, presentado por el PNUD; y

b) Pedir a los organismos bilaterales y de ejecución que compartan las evaluaciones del PNUD sobre el metilal, junto con información sobre otras alternativas, cuando presten asistencia a los países que operan al amparo del Artículo 5 para preparar proyectos para la eliminación del HCFC-141b en aplicaciones de espumas de poliuretano.

**Mundial: Opciones de bajo costo para el uso de hidrocarburos en la fabricación de espumas de poliuretano. Una evaluación para la aplicación en proyectos del Fondo Multilateral**

*Antecedentes*

120. El PNUD ha presentado a la 66ª reunión un informe técnico sobre opciones de bajo costo para el uso hidrocarburos en la fabricación de espuma de poliuretano: una evaluación para la aplicación en proyectos del Fondo Multilateral. El examen técnico completo se adjunta a este documento (Apéndice III).

121. En la 58ª reunión, el Comité Ejecutivo aprobó la validación/demostración de opciones de bajo costo para el uso de hidrocarburos como agente espumante en la fabricación de espumas de poliuretano en Egipto (decisión 58/31).

*Resumen ejecutivo*

122. El proyecto de demostración de opciones para el uso de hidrocarburos es diferente de otros proyectos piloto en cuanto a que se centra en la optimización de costos y rendimientos de una tecnología ya existente y ampliamente aplicada. Los altos costos limitan, de hecho, la tecnología de hidrocarburos a las empresas grandes, y han dado lugar, en forma indirecta, al amplio uso de HCFC-141b en empresas más pequeñas y/o menos sofisticadas. Si bien el umbral financiero para dichos proyectos ha aumentado recientemente debido a su bajo PCA, los costos de los equipos también han aumentado. Por lo tanto, las EPM solamente pueden recurrir a HFC indeseables desde el punto de vista ambiental o sistemas a base de agua con un rendimiento marginal, o bien esperar que la evaluación de nuevas tecnologías ofrezca opciones más satisfactorias.

123. El uso de tecnología de hidrocarburos no ha cambiado mucho en los últimos 20 años. Requiere equipos de premezcla y dosificación costosos, una zona de producción libre de explosiones y procedimientos de seguridad especiales. También, en muchos países, las formulaciones de los sistemas no han cambiado a lo largo de los años, aunque las mejoras en los aditivos y polioles y la opción de comezcla y más optimizaciones permitirían lograr mejores resultados con costos equivalentes o más bajos.

124. El proyecto de demostración se ejecutó en tres etapas, a saber: desarrollo de equipos, seleccionados por medio de procedimientos de adquisición normalizados por un proveedor de equipos seleccionado por medio de una adquisición normalizada; desarrollo de sistema a cargo de un proveedor de sistemas cualificado, incluidas pruebas en un fabricante de espumas o proveedor de sistemas local

dispuesto con la capacidad apropiada; y presentación de informes, que incluyó un taller interregional para divulgar los resultados, seguido de un informe final al Comité Ejecutivo.

125. Durante la ejecución del proyecto, el PNUD identificó opciones para: reducción de costos en la premezcla en el nivel del proveedor, que evitaría la necesidad de utilizar un premezclador junto con equipos auxiliares (p. ej., tanques de almacenamiento, tuberías); inyección directa de hidrocarburos, que también elimina la necesidad de utilizar sistemas de premezclador; e introducción de mezclas de hidrocarburos desarrolladas más recientemente, que permitirían densidades de espuma más bajas.

126. El equipo seleccionado fue un distribuidor de alta presión de tres módulos con capacidad para procesar sistemas completamente formulados, con inyección directa de agentes espumantes tanto inflamables como no inflamables. En los ensayos, funcionó bien para sistemas de HCFC (sistemas de base), sistemas de premezcla e inyección directa. En particular, el distribuidor ofreció una excelente capacidad de repetición; mezcla de tres componentes aceptable (futuros ajustes pueden mejorar el rendimiento); y alta eficiencia en la contención del agente espumante, lo que permite densidades de espumas más bajas. Como se muestra en el cuadro 7 a continuación, se seleccionaron seis sistemas diferentes. Los sistemas a base de HCFC-141b actuaron como sistemas de base, mientras que los isómeros de pentano reflejan las preferencias actuales del mercado. Todos los sistemas con pentano como agente espumante se evaluaron como sistemas completamente formulados (agente espumante incluido) y como sistemas parcialmente mezclados (agente espumante añadido como un tercer componente).

**Cuadro 7: Sistemas de espumación seleccionados para las pruebas**

| Agente espumante | Refrigeración comercial | Paneles discontinuos | Calentadores de agua |
|---|---|---|---|
| HCFC-141b | Sistema A | Sistema C | Sistema E |
| Ciclopentano | Sistema B | Sistema D | Sistema F |
| Pentano normal | Sistema B | Sistema D | |

127. Los resultados de las pruebas realizadas demostraron que:

a) Se confirma la estabilidad física y química de los sistemas de ciclopentano bajo condiciones estándar durante un periodo de hasta seis meses. Los sistemas de pentano normales no son estables después de un mes;

b) Para los sistemas de premezcla, dado que no se requiere un sistema de premezclador, pueden esperarse ahorros de costos de alrededor de 100.000 $EUA;

c) Si bien para la inyección directa no hay ahorros en el costo de los equipos, el diseño compacto podría permitir ahorros de costos en la disposición y el almacenamiento;

d) Si la densidad libre más baja puede “traducirse”·en una densidad aplicada más baja, pueden esperarse ahorros de explotación de alrededor del 6% y el 8% (o el 10% con inyección) en comparación con los sistemas a base de HCFC-141b. Sin embargo, pueden aumentar los costos de transporte;

e) Un factor k algo más elevado[1] (entre 5% y 8%) y una reactividad más baja muestran que el inyector del cabezal del distribuidor de espumas ha sufrido a causa de la introducción de un tercer componente. Si bien podrían lograrse mejoras por medio de un paquete de catalizador optimizado, se deberá considerar un nuevo diseño del cabezal de mezcla del distribuidor.

[1] La conductividad térmica para una unidad de espesor de material.

128. Si bien todas las afirmaciones técnicas se consideran universalmente válidas, las afirmaciones sobre costos se aplican únicamente a Egipto y deberían ajustarse para otras regiones u otros países. Aunque el PNUD ha identificado varias áreas en las que se requiere seguimiento (eficiencia del cabezal de mezcla, optimización del catalizador) se considera que los resultados actuales son significativos y justifican la publicación inmediata.

*Conclusión del revisor técnico*

129. El revisor técnico llegó a la conclusión de que el estudio ha verificado las propiedades físicas aceptables de productos de espumas rígidas para aplicaciones en refrigeración, paneles discontinuos y calentadores de agua usando sistemas a base de hidrocarburos premezclados así como dosificación directa de hidrocarburos; también ha verificado la estabilidad de los sistemas premezclados de ciclopentano durante un periodo de cinco meses. Continúan los estudios para verificar una vida útil mínima de seis meses. También ha demostrado que los sistemas de n-pentano no son adecuados para premezcla debido a la inestabilidad (separación de fase) del producto mezclado. El estudio ha demostrado el uso de una unidad de distribución de tres componentes diseñada para ofrecer flexibilidad de funcionamiento entre sistemas premezclados y de dosificación directa de hidrocarburos.

130. El estudio no verificó de forma adecuada la seguridad continua de las operaciones con los nuevos sistemas y equipos. Se deberían realizar otros estudios para generar datos que establezcan con claridad que las operaciones de mezcla de tres componentes cumplen los requisitos de seguridad, especialmente en cuando a la inflamabilidad, en el procesamiento tanto de sistemas de premezcla como de dosificación directa de hidrocarburos. Se debe proporcionar más información acerca de los requisitos de seguridad en cuanto a ventilación y supervisión durante el transporte y el almacenamiento de sistemas de polioles premezclados, incluidos los costos proyectados. Se debería llevar a cabo un análisis de costos para la conversión de estos sistemas de premezcla/inyección directa a fin de establecer el nivel de uso aproximado que aprovecharía este perfeccionamiento tecnológico.

## Observaciones de la Secretaría

131. El proyecto piloto de validación de opciones de bajo costo para el uso de hidrocarburos en la fabricación de espumas de poliuretano incluyó talleres para divulgar los resultados de los proyectos. Al respecto, se realizó un taller en Egipto (4 y 5 de julio de 2011) con los siguientes participantes: 11 proveedores de sistemas de 5 países (Egipto, los Emiratos Árabes Unidos, Sudáfrica, Brasil e Italia); 19 empresas fabricantes de espumas de Egipto; representantes de 5 países que operan al amparo del Artículo 5 (Brasil, Egipto, Sudáfrica, Turquía y los Emiratos Árabes Unidos); representantes del PNUD, el PNUMA y la ONUDI; y mayoristas de agentes espumantes del Brasil y Egipto; 3 fabricantes de equipos de inyección de espumas (multinacionales); y representantes de los cuatro principales fabricantes internacionales de poliuretanos. Los resultados del proyecto piloto se divulgaron durante el proceso de ejecución del plan de gestión de eliminación de los HCFC para varios países (Brasil, Nigeria, México), en reuniones con los interesados y visitas a compañías de espumas y proveedores de sistemas. Varias compañías de la mayoría de estos países han manifestado su interés y han enviado consultas.

132. La Secretaría pidió que se explicasen más detalladamente los posibles costos adicionales en que se incurriría en el nivel de las empresas con el uso de sistemas a base de hidrocarburos. En su respuesta, el PNUD explicó que los polioles premezclados de hidrocarburos son productos peligrosos calificados como inflamables. El almacenamiento de polioles en una planta debería ser por lo tanto adecuado para almacenar productos inflamables. Dado que la empresa anteriormente usaba polioles premezclados, los requisitos generales de espacio serían los mismos y las operaciones con espumas serían similares a aquellas cuando se utilizan hidrocarburos puros; por lo tanto, debería haber sistemas y equipos de

seguridad instalados. La principal diferencia es que no se requiere premezcla en el sitio y, por lo tanto, el usuario posterior no necesita contar con conocimientos acerca de la composición del sistema. La infraestructura a nivel de la empresa se simplifica, dado que se usa un componente químico menos (hidrocarburo puro) y se realiza una operación menos (premezclador y equipos auxiliares).

133. Considerando la necesidad de proporcionar información adicional sobre cuestiones relacionadas con la seguridad y los costos, conforme a lo sugerido por el revisor técnico, el PNUD llevará a cabo otras investigaciones relacionadas centradas en el ajuste de los conceptos de seguridad para cada uno de ambos enfoques (inyección directa, sistemas premezclados), las menores densidades libres observadas en los polioles premezclados y de inyección directa que podrían ocasionar densidades de producto más bajas (aceptables), optimización del cabezal de mezcla, extensión del enfoque de inyección directa a un modelo de retroadaptación rentable y concepto de costos basado en este informe. Los resultados de estas investigaciones de seguimiento se presentarán en un informe complementario que se presentará a la 67ª reunión.

<u>Recomendación de la Secretaría</u>

134. El Comité Ejecutivo pudiera:

a) Tomar nota con agradecimiento del informe titulado "Opciones de bajo costo para el uso de hidrocarburos como agente espumante en la fabricación de espumas de poliuretano: Una evaluación para la aplicación en proyectos del Fondo Multilateral", presentado por el PNUD; y

b) Pedir al PNUD que finalice las investigaciones adicionales sobre cuestiones relacionadas con la seguridad, densidades y optimización de equipos, y que desarrolle además un concepto de costos basado en polioles de hidrocarburos premezclados y que presente un informe complementario a la 67ª reunión; y

c) Pedir a los organismos bilaterales y de ejecución que compartan las evaluaciones del PNUD sobre opciones de bajo costo para el uso de hidrocarburos en la fabricación de espumas de poliuretano, junto con información sobre otras alternativas, cuando presten asistencia a los países que operan al amparo del Artículo 5 para preparar proyectos para la eliminación del HCFC-141b en aplicaciones de espumas de poliuretano.

**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)**<br>1.4.1 Attendance to financial and administrative workshop to harmonize the policies of UNEP and the GoP<br>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<br>1.4.3 Follow-up training of partner agencies and regional offices on database management and maintenance<br>1.4.4 Regional forum on the updates of the NCPP Project Implementation and other NCPP implementation requirements | <br>1<br>1<br>4<br>2 | <br>8,200<br>19,048<br>28,571<br>28,572 | <br>June 2012<br>3rd Quarter of 2012<br>3rd Quarter of 2012<br>June 2012-April 2013 | 10,000 |
| | 1.5 **Turn-over of training equipment to Training Institutes**<br>1.5.1 Conduct meetings with TESDA on the findings of the assessment on the training equipment conducted by NCPP-PMU<br>1.5.2 Conduct physical verification of training equipment nationwide<br>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<br>1.5.4 Preparation of documentary requirements and distribution of deed of donations | 150 sets<br>12<br>16 regions (1.5.2–1.5.3)<br>150 Training Institutions & 16 EMB Regional Offices | <br>286<br>11,905 | Jan -June 2012 (1.5.1–1.5.3) | 5,000 |
| | 1.7 **Preparation of Project Completion Report of overall implementation of the NCPP (for the period 2012-2014)**<br>1.7.1 Hiring of Individual Consultant for the preparation of PCR<br>1.7.2 Conduct of annual financial audit<br>1.7.3 Preparation/Finalization of reports (closing of books, meetings with partner agencies, TWG, etc.) | <br>1<br>2<br>2 | <br>4,762<br>4,762<br>1,429 | <br>January-April 2013<br>2012-2013<br>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<br>2.1.1 CY 2009&2010 (HCFCs)<br>2.1.2 CY 2011-2013 (CFCs and HCFCs) | 2<br>4 | 47,619 | 2nd Quarter of 2012<br>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<br>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<br>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<br>2.5.1 Conduct of compliance monitoring of completed investment projects<br>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. | 5 (Phase 2)<br>16 | 4,762<br>4,762 | 2012-April 2013<br>2012-April 2013 | 5,000 |
| | 2.6 Implementation of the amended IRR of PD 1572 specifically on the accreditation of service shops<br>2.6.1 Provide regulatory support to DTI and LGUs on the service shops' full compliance to the accreditation requirements<br>2.6.2 Monitoring of service shops nationwide in coordination with DTI and BPLO | 16 DTIs<br>2521 | 7,143<br>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**<br>3.1.1 Hiring of a Technical Expert/Consultant<br>3.1.2 Coordination meetings with core group consist of 5 technical groups/associations that would prepare the draft COP<br>3.1.3 Conduct of Regional consultations nationwide on the updated Code of Practice | 1<br>1<br><br>3 | 7,143<br>4,286<br><br>21,426 | 2nd Quarter of 2012<br><br><br>3rd and 4th Quarter of 2012 | 15,000 |
| | **3.2 Assessment of Service Shop Voucher Grantees**<br>**3.2.1** Hiring of Regional Coordinators<br>3.2.2 Conduct of actual survey<br>3.2.3 Hiring of M& E Consultant for the assessment of Training Institutes and Service Shop grantees (85% audit)<br>3.2.4 Regional consultation on the draft assessment report<br>3.2.5 Finalization of assessment report | 10<br>1,339<br>1<br><br>4<br><br>1 | 12,753<br>25,505<br>3,524<br><br>21,423 | 3rd Quarter of 2012<br><br>4th Quarter of 2012 | 5,000 |
| | 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<br>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<br>3.5.1 Training supplies and materials<br>3.5.2 Travelling expenses<br>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:<br>3.6.1 Conduct coordination meetings with LTO on the preparation of assessment report on the compliance of motor vehicles to refrigerant type<br>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<br>3.6.3 Conduct of MAC random roadside inspection by a composite team on a quarterly basis | 10<br>108<br>80 | 1,190<br>205,714<br>9,524 | 2nd Quarter of 2012<br>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<br>4.1.1 Conduct coordination meetings with DELSA on the CTS scheme to cover other regions<br>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.**<br>1. 10 units of 1 tonne tank/cylinder<br>2. 4 units Recovery Machine<br>3. 1 unit Transfer Pump<br>4. 20 units (100 KG Cylinder)<br>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**<br>- Amended CCO for ODS<br>- Revised Code of Practice<br>- Updated NCPP Primer including HCFC<br>- Brochures and leaflets<br>- Tarpaulins/Posters<br>- Newsletters<br>- Web Pages that highlight service shop benificiaries<br>- E-learning training modules<br>- Social Networking<br>- 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

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

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

## 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$^o$C and 30$^o$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 56$^{th}$ 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 58$^{th}$ ExCom | Evaluation of cost saving options |
| Methyl formate | Approved at the 56$^{th}$ ExCom | Technical validation of a commercial available product |
| Methylal | To be submitted to 58$^{th}$ 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 57$^{th}$ 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$) | | |
|---|---|---|---|---|
| | | INDIVIDUAL | SUB-TOTAL | TOTAL |
| | **PHASE-I – DEVELOPMENT/OPTIMIZATION/VALIDATION/DISSEMINATION** | | | |
| 1 | Preparative work<br>Project Preparation<br>Technology Transfer, Training | <br>30,000<br>25,000 | 55,000 | **464,200** |
| 2 | System Preparation<br>Development (17 applications) @ 5,000<br>Optimization (17 applications) @ 3,000<br>Validation (18 applications) @ 2,000 | <br>85,000<br>51,000<br>36,000 | 172,000 | |
| 3 | Laboratory Equipment<br>K-factor tester US$ 10,000<br>Refractometer 5,000<br>Brett mold 5,000<br>HP laboratory dispenser 50,000<br>Sprayfoam/PIP dispenser 20,000<br>pH tester 5,000<br>Abrasion tester 25,000<br>Cell gas analyzer 20,000<br>Laboratory Safety | <br>10,000<br>5,000<br>5,000<br>50,000<br>20,000<br>5,000<br>25,000<br>20,000<br>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<br>1 Blender<br>1 Tank for Methylal<br>Safety measures<br>Contingencies (10%) | <br>50,000<br>20,000<br>25,000<br>9,500 | 104,500 | |
| 2 | Discontinuous Operations (12)<br>14 Retrofits @ 15,000<br>14 Trial Programs @ 3,000<br>Contingencies (10%) | <br>210,000<br>42,000<br>25,200 | 277,200 | |
| 3 | Continuous Operations (3)<br>3 ex proof metering systems @ 15,000<br>3 ventilation units @ 25,000<br>3 sensor systems @ 15,000<br>3 grounding programs @ 5,000<br>Contingencies | <br>45,000<br>75,000<br>45,000<br>15,000<br>18,000 | 198,000 | |
| 4 | Peer review/safety audits | | 50,000 | **629,700 + IOCs** |
| 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**

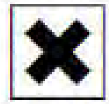
| TASK | MONTH* |
|---|---|
| (a) Project document submitted to beneficiaries | 2 |
| (b) Project document signatures | 3 |
| (c) Bids prepared and requested | 3, 9 |
| (d) Contracts Awarded | 3, 9 |
| (e) Equipment Delivered | 4, 11 |
| (f) Training Testing and Trial Runs | 4, 12 |
| (g) Commissioning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

* As measured from project approval

# ATTACHMENT II:
# MATERIAL SAFETY DATA SHEET/OSHA GUIDELINES

| | |
|---|---|
| **MATERIAL SAFETY DATA SHEET** | Page : 1<br>Revision nr : 5<br>Date : 30/9/2005 |
| **METHYLAL TECHNICAL GRADE** | Supersedes : 20/2/2004<br>**L-9307**<br>www.lisam.com |

Highly flammable



Harmful

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## 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. |

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| | L-9307 |

## 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 |

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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<br>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.<br>R20/21/22 - Harmful by inhalation, in contact with skin and if swallowed.<br>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. |

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**EMERGENCY : +32 (0)70 245 245**

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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.

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**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.

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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### RESPIRATORY PROTECTION FOR METHYLAL

| Condition | Minimum Respiratory Protection* Required Above 1000 ppm |
|---|---|
| Vapor Concentration | |
| 10,000 ppm or less | Any supplied-air respirator.<br>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.<br>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.<br>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

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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<br>NA | NA | Oral<br>(gavage ?) | NA | Undiluted | 1 | 6,950 | NA | May 1983 | Municipal Public Health Department, Moscow<br>USSR |
| 2 | Rat<br>NA | NA | Oral<br>(gavage ?) | NA | Undiluted | 1 | 9,070 | NA | May 1983 | Municipal Public Health Department, Moscow<br>USSR |
| 3 | Rat<br>NA | Total : 8 F<br>2 F per dose | Oral<br>(gavage ?) | 1,000<br>2,000<br>3,980<br>7,950 | Undiluted | 2 | > 7,950 | No mortality up to 7,950 mg/kg | Dec. 1968 | Dow Chemical Company<br>USA |
| 4 | Rat<br>Wistar | Total : 50<br>5 M + 5 F<br>per dose | Oral<br>(gavage) | 1 ml/kg bw<br>2 « »<br>4 « »<br>8 « »<br>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<br>No gross pathology changes up to 8 (males) or 2 (females) ml/kg bw | Dec. 1982 | Bushy Run Research Center, PA<br>USA |
| 5 | Rabbit<br>NA | NA | Oral<br>(gavage) | 4560<br>5700 | Diluted in water | 4 | 5,700 | Mortality :<br>1/5 at 4560 mg/kg bw<br>4/7 at 5700 mg/kg bw | 1932 | University of California Medical School, San Francisco<br>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<br>NA | NA | Topical (ocular instillation) | 1 | Undiluted | 2 | Unwashed : moderate to severe conjonctival irritation<br>washed : moderate conjonctival irritation | Dec. 1968 | Dow Chemical Company **USA** |
| **15** | Rabbit<br>New Zealand | Total : 12<br>6 females per dose | Topical (ocular instillation) | 1 | Undiluted<br>0.01 ml/eye<br>0.1 ml/eye | 3 | 0.01 ml : minor irritation of conjunctivae<br>0.1 ml : minor corneal and iridal injury. Minor to moderate conjunctival irritation | Dec. 1982 | Bushy Run Research Center, PA **USA** |
| **16** | Rabbit<br>New Zealand | Total : 6<br>3 M + 3 F | Topical | 1 | Undiluted 0.5 ml<br>4 hour exposure | 3 | No cutaneous reaction | Dec. 1982 | Bushy Run Research Center, PA **USA** |
| **17** | Rabbit<br>New Zealand | Total : 6<br>2 M + 4 F | Topical | 1 | Undiluted 0.5 ml<br>4 hour period | 9 | Slight transient erythema<br>Primary irritation index (PII) = 0.42/8 | Nov. 1989 | Springborn Laboratories, Ohio **USA** |
| **18** | Rabbit<br>NA | NA | Topical | 10 on intact skin<br>3 on abraded skin | Undiluted | 2 | Intact skin : none to slight exfoliation<br>Abraded skin : slight hyperemia and exfoliation | Dec. 1968 | Dow Chemical Company **USA** |
| | | | | 10 on intact skin<br>3 on abraded skin | 10 % solution in Dowanol DPM | 2 | Intact skin : none to moderate exfoliation<br>Abraded skin : slight hyperemia and exfoliation | Dec. 1968 | Dow Chemical Company **USA** |

**NA : Information not available**

## 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.<br><br>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.<br><br>Water intake markedly higher than controls during Days 8 to 19 post coitum. | No changes considered to be related to exposure to methylal.<br><br>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 | Microbiologi cal 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 | Docu-ment ID | Results | Date | Laboratory |
|---|---|---|---|---|---|---|---|---|---|
| **28** | Delayed cutaneous sensitization maximization test | Guinea pig Dunkin-Hartley | Total 30 10 M + 10 F treated group<br>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

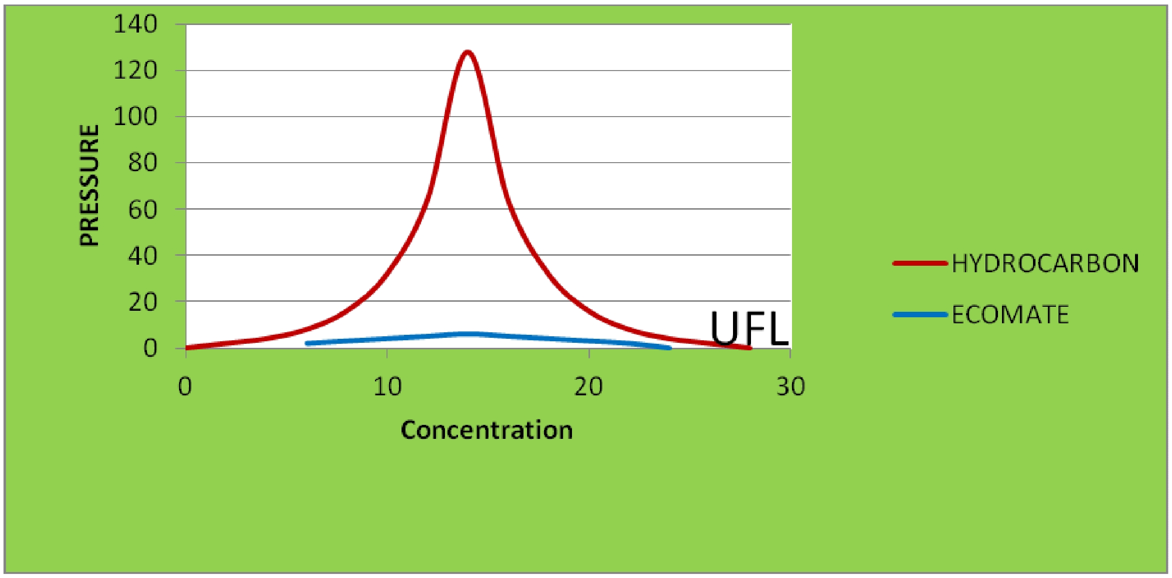
**Combustibility** - a blowing agent is commonly stored and processed as a liquid but turns into a gas as part of the foam expansion, due to the exothermic reaction between water and isocyanate (and to a lesser extent polyol and isocyanate), expanding the still liquid reaction mixture and filling the 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

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BELGIUM
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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

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<br>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.<br>R20/21/22 - Harmful by inhalation, in contact with skin and if swallowed.<br>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.



**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.

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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.<br>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.<br>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.<br>Any escape self-contained breathing apparatus. |

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

# 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

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.

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,

Robson C. Balbinot

Nome: ROBSON COLOMBO BALBINOT

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: Claudio 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

Politech Poliuretanos Indústria e Comércio Ltda – Rua Dona Alzira , 433 – Bairro Sarandi – Cep: 91110-010 – Porto Alegre – RS – Brasil – Fone/Fax: 00- (51)-3344-6909 e-mail: vendas@politech.ind.br

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.

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 Rigida 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



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

R. Estado do Amazonas, 609 • CEP 03935-000 • São Paulo - SP
vendas@isar.com.br • www.isar.com.br
Vendas: (11) 2107-0488
PABX: (11) 2107-0499

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

Poliuretanos Brasil Ltda - www.poliuretanosbrasil.com.br
Rua Moacir da Silveira, 326, - Santana de Parnaiba - SP
CEP: 06516-050 telefone: (011) 41512405 - contato@poliuretanosbrasil.com.br

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

M A R C H 2 0 1 2

# Table of Contents

## 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:

| Blowing Agent \ Application | 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 67$^{th}$ 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$^0$C 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 $67^{th}$ 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)**.

[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 (>$30^0$C) 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**

- o 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.
- o 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.
- o The acoustical alarm shall be a minimum of 85 Db, or at least 15 Db over plant noise level.
- o The visual alarm shall be in the pouring area.
- o The first alarm shall be for warning purposes only.
- o The second alarm shall shut down the pouring operation and the pentane supply, while increasing the process exhaust.
- o The system shall have an independent power back-up.
- o An auxiliary portable gas sensor with calibration unit shall be kept on site.

**Exhaust System**

- o 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.
- o The system(s) shall have a two stage capacity and back-up power.
- o The system(s) shall be interlocked with the sensor and alarm system.
- o The system(s) shall have an independent power back-up.

**Grounding**

- o All equipment in areas where CP emissions or leakage can occur shall be connected to a central electrical grounding system.
- o The grounding shall conform to internationally accepted specifications e.g. NFPA 77.

**Procedures**

- o The enterprise shall provide the necessary operational safety and emergency response instruction and training to staff and personnel involved in the operations using cyclopentane.
- o A Safety Manager shall be appointed in the factory. The manager will receiver appropriate training and education and be properly certified.
- o Hazardous areas shall be clearly marked by signs indicating the Area Zoning.
- o Piping shall be color coded.
- o No smoking shall be allowed in the factory and its immediate surroundings. The no smoking policy shall be properly marked by signs.
- o 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.
- o A Safety Manual shall be developed and maintained. The manual should as a minimum address:
    - o Safety Organization and Responsibilities
    - o Standard Procedures for Work in Hazardous Areas
    - o Response to Emergency Alarms
    - o 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:**

___

**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 $^oC$ | 32 $^oC$ |
| LEL/UEL | 2.2-19.9 % | 7.6-17.7 |
| Vapor pressure | 400 mm Hg @ 20 $^oC$ | 593 mm Hg @ 25 $^oC$ |
| Lambda, gas | Not available | 10.0 mW/m.k @ 25 $^oC$ |
| Auto ignition | 235 $^oC$ | >200 $^oC$ |
| Specific gravity | 0.821 @ 20 $^oC$ | 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 ($^0C$) | -19 | >15 <32 | >25 | >10 <30 |
| Gas Conductivity (mWm$^0$K at 10 $^0C$) | 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).

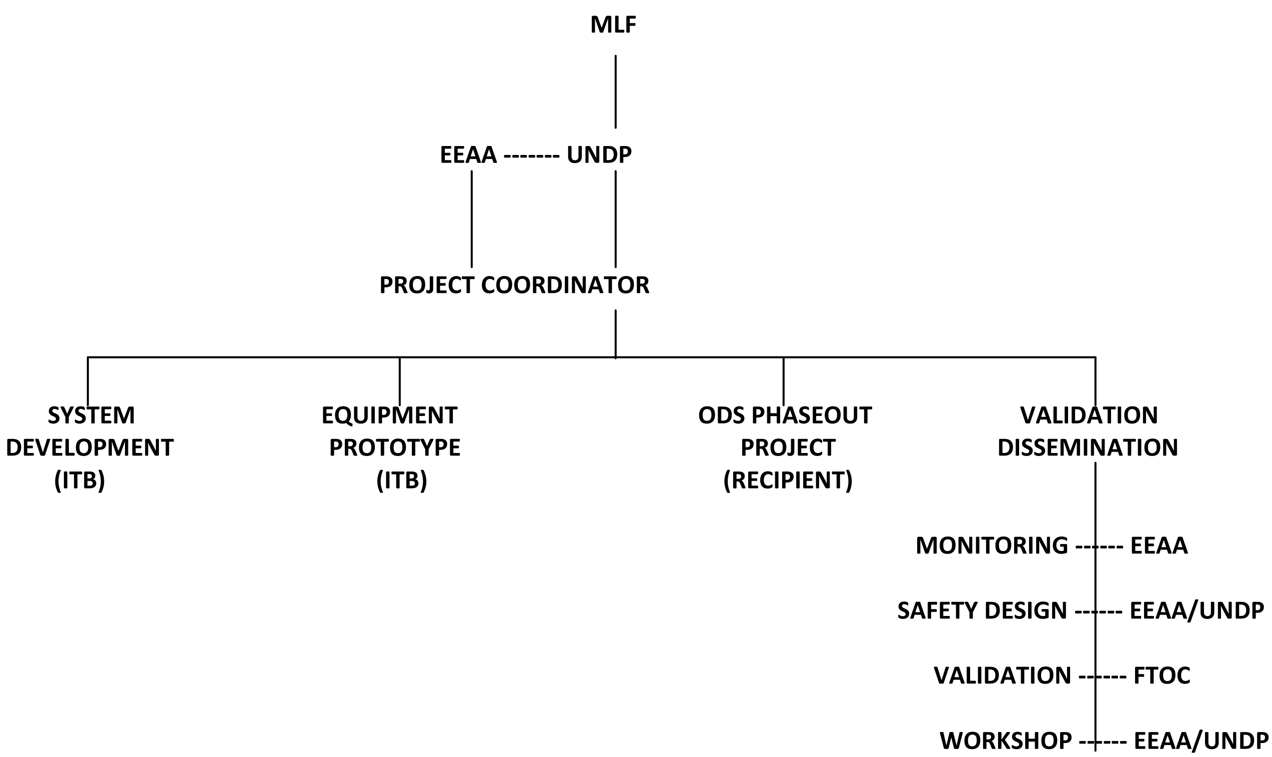
8. **Equipment Development:** as before, UNDP will contract this out to a qualified equipment supplier, following standard procurement procedures.

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<br>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<br>- safety audit<br>- design study for centralized HC blending<br>- 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:

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.

[1] Presentation to the UNDP workshop on "Innovative Low Cost Hydrocarbon Technologies" in Cairo, Egypt July 4, 2011

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.

All equipment is built according to ATEX 94/9/EC directives European Standard and in conformity with II 2 Gc IIB T4.

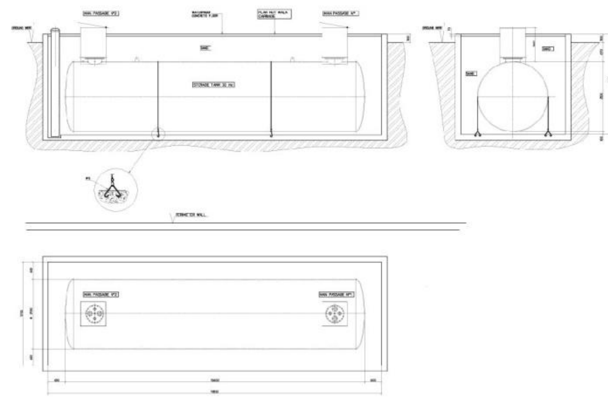
Activities required to introduce HCs in a production facility vary according to geographical area, size of the enterprise, type of production and conditions of the existing facilities.

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.

<u>The HCs storage farm</u>

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.

<u>The mixing head</u>

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.

## <u>The retrofit of the equipment polyol line where applicable</u>

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.

<u>The retrofit of the polyol line with line replacement</u>

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.

<u>The auxiliaries equipment</u>

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

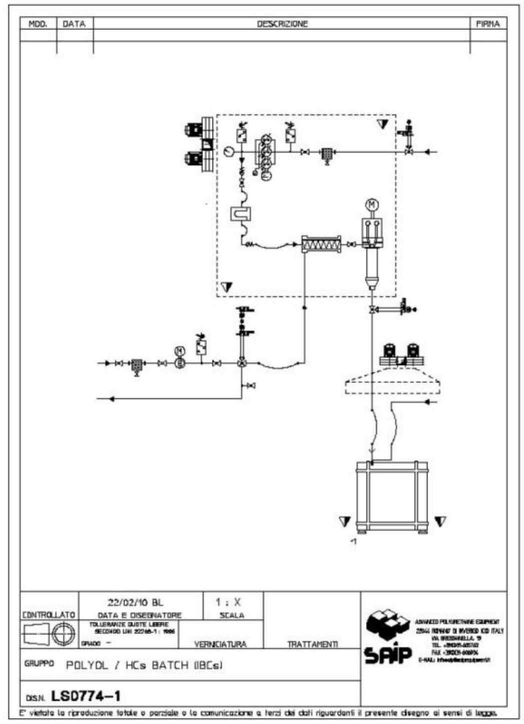
Fully formulated HCbased polyols can be supplied in drums or IBC tanks as readytouse PU systems.


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.

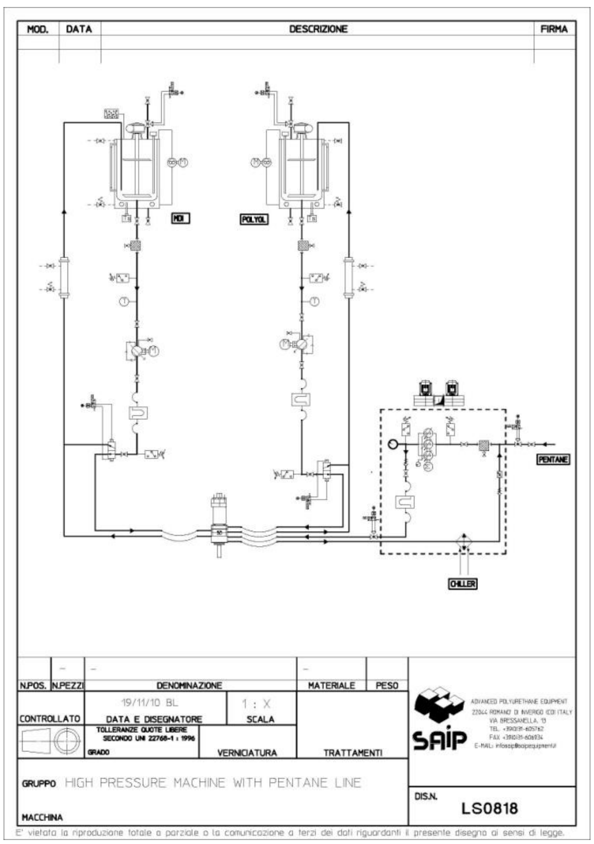
For the third stream injection the following equipment is needed:

- 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 :

<u>The isocyanate line</u> in a standard configuration

- No enclosure and ventilation
- No detection system
- No Ex – proof components

<u>The polyol / HC blend line</u>

- 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

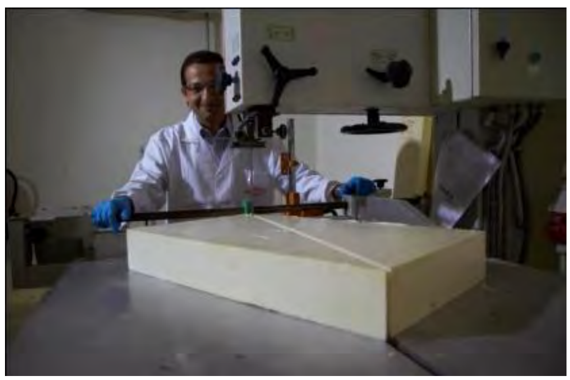
Picture 5,6: Extraction from brett mold, injection in jumbo mold and extraction of produced foam



**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.

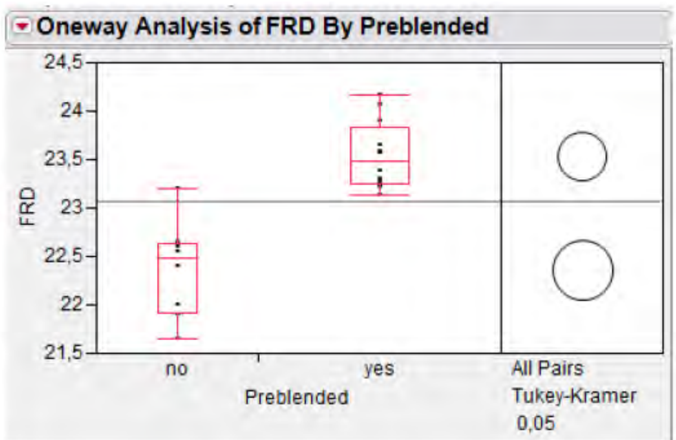



Chart 1: Free rise density comparative analysis third stream ( left) vs preblended (right)

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.

<u>Effect of type of addition: third stream vs pre-blended</u>

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.

<u>N-pentane vs c-pentane comparison</u>

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.

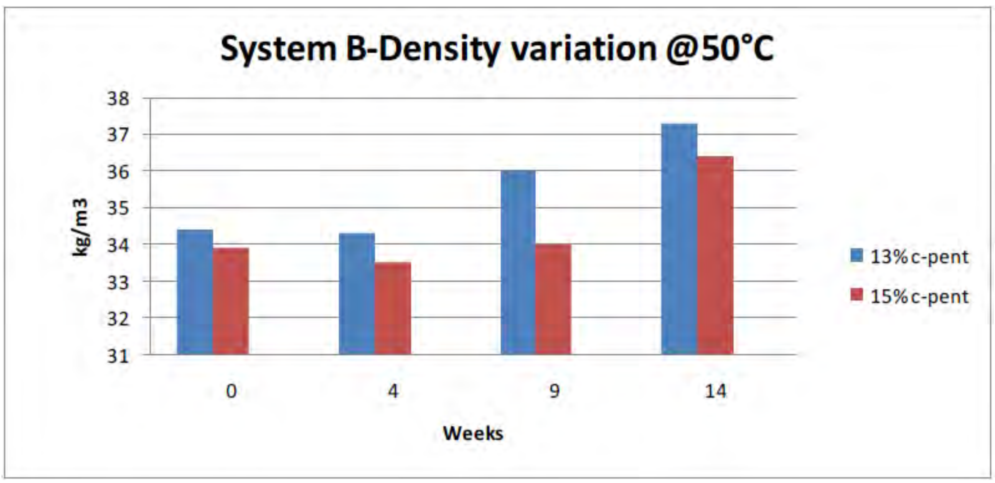
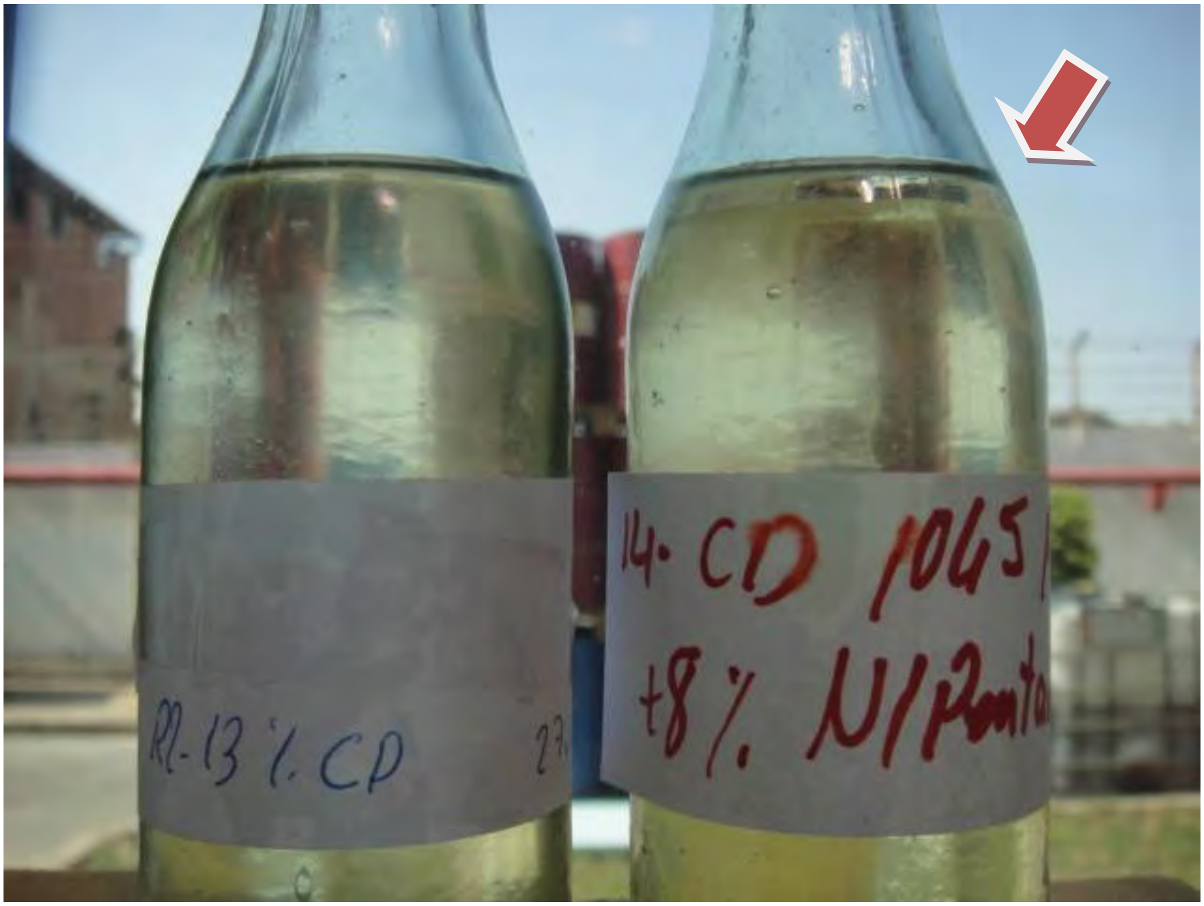



Chart 2: evolution of free rise density along time at 50°C aging temperature for polyol blend of System B fully formulated with c-pentane.

It is clear how the behavior of fully formulated blends would be not only formulation dependant but also handling and storing conditions highly dependent.

n-pentane pre-blended polyols shelf- life.

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.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**CONCLUSIONS**

Outcome of this project according to initial objectives can be summarized as follows:

- NEW DISPENSING UNIT:

    - o 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

    - o 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.
    - o 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 .
    - o 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.
    - o 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.
    - o 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

    - o 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.
    - o 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:

    - o 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.
    - o This comparison has to be considered valid for other countries as well
    - o 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.

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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℃, and by performing reactivi ty 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℃ 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

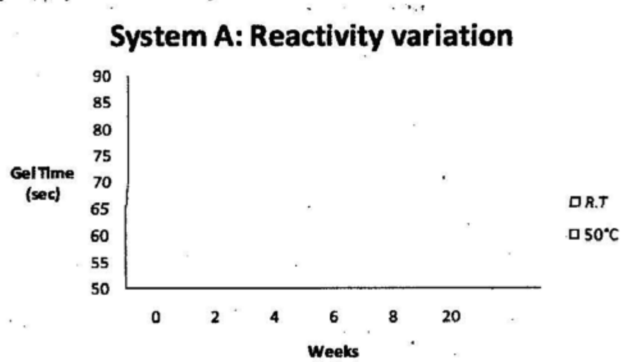
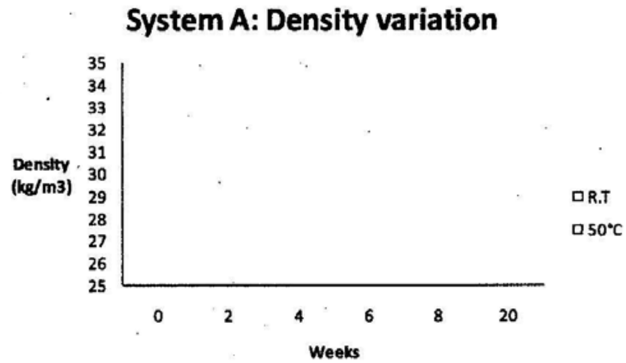



Figure 2: System A free rise density variation.



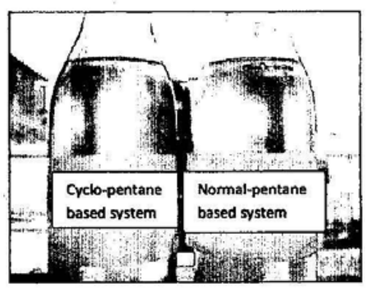

**System B: Normal-pentane based system for Commercial appliance**

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 alrea dy 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.