

# EP

# الأمم المتحدة

Distr.  
GENERAL

UNEP/OzL.Pro/ExCom/66/17  
22 March 2012

ARABIC  
ORIGINAL: ENGLISH

برنامج  
الأمم المتحدة  
للبيئة



اللجنة التنفيذية للصندوق المتعدد الأطراف  
لتنفيذ بروتوكول مونتريال  
اجتماع لسان ادس لوس تون  
هوتويال، 16-02 أيلول/يونيس ان 0210

تقري عن تهيئ المشروع اتل م وافق عل يابش روقبل ي غ محددة

## مقدمة

1 طلبت الأمانة من الوكالات الثنائية والمنفذة أن تقدم إلى الاجتماع السادس والستين التقارير المرحلية المعلقة بشأن تنفيذ المشروعات، حيث ترد شروط إبلاغ محددة في اتفاقات ومقررات اللجنة التنفيذية ذات العلاقة المتخذة بين الاجتماع التاسع والخمسين والاجتماع الخامس والستين.

2 تشمل هذه الوثيقة تقارير البلدان التالية، التي قدمت بعد موعد نهائي بثمانية أسابيع من الاجتماع الخامس والستين ولكن الأمانة لم تتمكن من استعراضها: بوركينا فاسو (تقرير تحقق من خطة إدارة إزالة نهائية)؛ الصين (تقرير تحقق ومرحلي لقطاع المذيبات)؛ كوت ديفوار (تقرير تحقق من خطة إدارة إزالة نهائية)؛ أندونيسيا (تقرير تحقق لخطة وطنية للإزالة)؛ فيرغيزستان (تقرير مرحلي عن خطة إدارة إزالة نهائية)؛ ساو تومي وبرنسيبي ((تقرير تحقق من خطة إدارة إزالة نهائية)).

## هيكل الوثيقة

3 قامت الأمانة بتجميع التقارير المرحلية في ستة أقسام:

القسم الأول: خطط وطنية للإزالة وخطط إدارة الإزالة النهائية

القسم الثاني: خطط إزالة قطاعية

القسم الثالث: الدعم المؤسسي

القسم الرابع: حشد الموارد من أجل الفوائد البيئية

القسم الخامس: مشروعات تدمير المواد المستنفدة للأوزون

القسم السادس: مشروعات استثمارية وبيانية للمواد الهيدروكلور وفلوروكربونية

## الأول خطط وطنية للإزالة وخطط إدارة الإزالة النهائية

4 قدم اليونان واليابان والكويت والهند والبنين والبرازيل والولايات المتحدة:

(أ) لبرازيل: خطة وطنية. إزالة المواد الخطرة وفلوروكربونية وقطري تخرج عام 2020 تحقيق مرحلي لعام 2000 وخطة عمل عام 2000 (اليونان واليابان)

(ب) بورنيو: خطة وطنية وتحقيق من تنفيذ خطة إدارة إزالة نهائية (2022) (اليونان واليابان)

(ج) كوت ديفوار: تحقيق من تنفيذ خطة إدارة الإزالة نهائية (2007-2008) (اليونان واليابان)

(د) لندونيسيا: لخطة وطنية للإزالة التي تحقق من أداء لفترة 0222-0222 (اليونان واليابان)

(هـ) فيرغيزستان: تحقيق مرحلي عن خطة إدارة الإزالة نهائية (الشريحة الثالثة والثالثة) (اليونان واليابان)

(و) ليلي: لائحة وطنية لإزالة المواد الخطرة وفلوروكربونية (202-0222) تقرير تحقيق وخطة عمل لعام 2000 (اليونان)

(ز) ساوتومي وبرنسيبي تقرير التحقيق من تنفيذ خطة إدارة الإزالة (2022-0222) (اليونان)

5. لتعرضت الأمل لتقارير الـ مقدمة في ضوء اقتراحات لمشروعات الأضرار التي باتت المواد لم تتفقد للأوزون من الحكومات المبرمة عملاً المادة 2 من بروتوكول فينتيال والتقرير المرجعي لتاريخه السابقة لتقديمه إلى اللجنة التنفيذية للمقررات ذات العلاقة التي بحثها اللجنة التنفيذية وإجماعات الأطراف.

**لبازيل: خطة وطنية لإزالة المواد الكلوروفلوروكربونية (تقرير تحقيق عام 2012) تقرير مرحلي عام 2011 وخطة عمل عام 2010 (البيرو)**

6. وافقت اللجنة التنفيذية في اجتماعها السابع والثلاثين في لائحة الوطنية للإزالة من أجل الإزالة التامة لتدهلاك المواد الخطرة وفلوروكربونية في البرازيل بحلول 1997 أي قبل أول ثلثي 2002. وقد تم تمويل موافق في 26,700,000 دولار أمريكي ووافقت اللجنة التنفيذية في لائحة الوطنية وللجنة الوطنية للإزالة في الاجتماعات مع ولائيين. وطبقت اللجنة أيضاً لتحقيق سنوي من لائحة الوطنية لإزالة المواد الخطرة وفلوروكربونية في البرازيل، حتى يقدم التحقيق من الأضرار عن عام 2002. وطبقت اللجنة التنفيذية في الاجتماعات الثلاث والستين للجنة التنفيذية من حكومة البرازيل من عدة لوائح، أن تقتصر على تقرير تنفيذي سنوي لتقديمه إلى اللجنة التنفيذية في أول اجتماع للجنة التنفيذية لكل سنة حتى يتم من لائحة الوطنية للإزالة. وقد تم تمويل في لائحة الوطنية للإزالة من الأضرار والسياسة التي نتجت عنها من الأضرار عن عام 2000 ولتلك خطة تنفيذية سنوية لعام 2000.

### تقرير التحقيق

2. بين تقرير التحقيق أن البرازيل لم تلتزم بتطلبات الاتفاقية من حكومة البرازيل وللجنة بشأن إزالة المواد الخطرة وفلوروكربونية في عام 2002. في عام 2002، كان لدى البرازيل صفر من الواردات وقدر 2..0 طن من قدرات لتفاد الأوزون من الصادات من المواد الخطرة وفلوروكربونية.

### تقرير المرجعي عن عام 2000

2. في قطاع خدمة للتعبئة وتوزيع الألبان التي تم مشاؤها ويوجد مركز لتفحص لاجي عمل الأنفي من طينة جنوب البرازيل (توزيع) وتم إنشاء آخر موقت خزين. وتم تركيب 42 وحدة لإعداد التدوير في عام 2000. تم تجهيز بحال مع 25 مع 05 نفعية. وتم ايجار بينطين عمليين لاقبال غرف تبخير من المواد الخطرة وفلوروكربونية، وبدأت عملية لئاقص الشراء. وتم ايجار 4 منشآت لئيان إعادة التجهيز أو إحلال معدات لتبخر لتجارية وللهدف للشراء. وأجرائت وتوزيع وتجهيزت لئاقبال نقل من أجزة الألبان قبل جرات لفئة للخطرة وفلوروكربونية لئيبطال ووزعت وتم إعداد لتبخر.

### خطة التنفيذ السنوية لعام 2000

2. بالنسبة لعام 2000 في خطط عدد من الأشرطة لئاقب من لائحة الوطنية للإزالة: إنشاء وطب معدات عدد 05 وحدة إعدادت قبل تنفيذ خطط عمل الخطرة وفلوروكربونية -00 في شمال البرازيل مع أدوات لترداد لتفخين لتبخر يمكن لتبخرها مع لأمواد التي تدور للخطرة وفلوروكربونية وبعض لأمواد التي تدور للخطرة وفلوروكربونية وطب إحلال غرف تبخير لتبخرها مع لأمواد التي تدور للخطرة وفلوروكربونية؛ إعدادت لئيان أو إحلال 02 وحدة أخرى من لأمعدات لتجارية لئيبطال للخطرة وفلوروكربونية -00؛

التهاء من معيارين يشأن حدود مهية ليدروفلووروكيبون تمتحيين نموذج معياري المتجارة لوطي فنظام اللوقبة لغير اللثووفلووروكيبون، وإدراج أدوات تتببع لسوطل تللبريد للصتردة وللمعتدويرها ولا متصلحة ؛ الوغلق للشغلي والاطلي للشروع.

## تحقيقات الأملة

### تقرير التحقيق

02 إنبلييلات لقدم هي تقرير التحقيق تتفق مع عينات لتبهلك لامادة 2 لتي قدمها للبرازيل لى أمله الأوزون.

### الأموال الوافق لحيها والأرصدة

00 ضهي سمبركلون الأول 0200 تم صرف جيع للمويل بلوثناء بملغ 0 222 542 دولار أمريكي (2 في لاهة). ويلغ ليوون هي أن لارصيد للتحقيق قديم التزامبه للأشطة لاختطة لوطية للإزالة. هوج دلشاطين تآزرات متضامة معنأشطة لامواد ليدروفلووروكيبونية ولكن ليس لها ابتباط إزالة أي من لامواد ليدروفلووروكيبونية معها، أي، تبدير اللوقبة لغير مهية للبعات اللثووفلووروكيبون، وتحيين إدارة المخرجات للنتيجة عن الالترداد. ولثم كان ملغن، أخذت مذلت آزراتفي الاضبارفي خطة إدارة إزالة لامواد ليدروفلووروكيبونية للبرازيل لتي تمت لامفلة لحيها في الاجتماع الاربع والستين.

### خطة لتفذي السن هي مل عام 0200

00 طبت الأمله أيضا مني دا من لامفومات عن لامعدات لتي يجرى شراؤه للشركاطل غير قومتوسطة لاجحفي قاطع تللبريد لتجارة. وأخطر ليوون هي أن لامعدات ستكون قطة لغير تلثوول لوجيات خلية من لامواد لامتنفدة للأوزون.

0. لاحظت الأمله أن لتقرير لمرلحي قديم أضيها انات عن ليدروفلووروكيبون -00 ومركز لتيرداد وإعادتدهور اللثووفلووروكيبون وتلارات مركز الالصلاح لى أنفي عام 0200 قامت لمرکز بمعالجة مقبايرص غيرة من اللثووفلووروكيبون -00 ولإيدروفلووروكيبون -00. بلقارن بعام 0222. هبدو أن قدار اللثووفلووروكيبون -00 لالعمل لحي مركز الالصلاح قدل قبض من 4.2 طرفي عام 0202 لى 0.2 طرفي عام 0200 معين ما زاد قدار ليدروفلووروكيبون -00 لى 02.4 طرفي عام 0200 من 06.2 طرفي عام 0202. هلمن نفسير معدل للالترداد لقبض للثووفلووروكيبون -00 بوسطة إحلال معدات تللبريد لقطامة لغير اللثووفلووروكيبون ولثللك تحيق أن لمحاب لامعدات للصناعة للغيرة لامتخدم للثووفلووروكيبون -00 يخنزون للثووفلووروكيبون لأغراض طييلة. وتلثوق الزيادة في معدلات سراترداد ولسصلاح لامواد ليدروفلووروكيبونية بلأحدود لاموضوعة لغير زيادة لتبهلك لامواد ليدروفلووروكيبونية لتي وضعها لحوكمة للبرازيل في سراق خطة إدارة إزالة لامواد ليدروفلووروكيبونية. وزادت لسعار ليدروفلووروكيبون -00 لأخا بولاي 2. لى 42 في لاهة ومنثم لمبحت أعم السراترداد ولسصلاح سوطل تللبريد لليدروفلووروكيبون -00 صلأ ققصداي.

04 قدم ليوون هي مني دا من لامفومات سراتجدة لطلب فطريل لكشتر عن مدى قدرة الأشطة لامخطة ل عام 0200 في المساهمة في لضاط لغير لتبهلك صفر من اللثووفلووروكيبون وهيير إزالة لامواد ليدروفلووروكيبونية هي للبرازيل. هتأاح اللثووفلووروكيبون وقطف للبرازيل من خلال يكل إحلال لامعدات وأشطة للالترداد وإعادتدهور والالصلاح. وهذا اليلكل هيفرن وعية عليها من إعانتدهور ولسصلاح

للثيووفلوروكيبون للمعدات حتى يتمكن من إصلاحها (اقتصر داي أوتقيا) من لتيبدال أو إعادة تجهيز المعدات للقائمة  
 في الثيووفلوروكيبون. إن الثيووفلوروكيبون لا يتردد من إحلال غر فستلبيد والمعدات لكجارية للصغيرة لا  
 ي يمكن إعادة تدويره لضم من نطق الهيير وقصص مخاطر لكجارية لغير المشروع فحسب بل أيضا في ريبيل ذي  
 فاعية للتألف من هبة للثيووفلوروكيبون له المكلفة الإلتزام لعلمي فخصصة. فيمكن أيضا ليلك للملترداد وإعادة  
 نلدوير والاشتغال للمركب أن يزن اول للمواد ليدروفلوروكيبونية وبعض للمواد ليدروفلوروكيبونية.  
 والتهاء من للمعيار للثيووفلوروكيبون حدوت هبة للثيووفلوروكيبون في قطاع تلبي ليلتجاري ييش مل أيضا حدوت هبة  
 للمواد ليدروفلوروكيبونية. إن تسمين ل نموذج معيار ليلتجارية لوطي قبي للثيووفلوروكيبون "يفر أداة  
 تتبعلس وطل للمتلبيد للصتردة والمعدودويها والمصنلح وتترصد هذه الأداة لكجارية لوطية يتوفر مقيم اتفسي  
 لوقت الليلب لى اللسلطات فيمكن تكرارها لرصد للمواد ليدروفلوروكيبونية والمواد  
 للثيووفلوروكيبونية.

توصية الأملة

05 قهرغب لكجيرة للتقنية أنتن طرفي:

(أ) الاحاطة في مابنقير لكجيرة ل عام 0202 قدير للتقيد للسنوي ل عام 0200 لكخطة لوطية لإزالة  
 للثيووفلوروكيبون في لهرائيل؛

(ب) توافق في خطة للتقيد للسنوي ل عام 0200؛

(ج) أنت طلب لى ليوون يبي أني واصل الإبلاغ عن التقيد في خطة لوطية للإزالة للهرائيل بينم  
 تقديم هذه للتقير في اللتزام روفي جداولتسق لضع اى لكجيرة ليلتحت ليلند (2) (من جدول الأعمال؛

(د) أنت طلب من حكومة لهرائيل و ليوون يبي، جرد لتهاء لكخطة لوطية للإزالة، تقيد مقير لتهاء  
 المشروع بطبق للشكل الملائم في اللتزام ل خامس والسنين.

**هوركين فسلن تقري ريتحقق ضمنها ذي خطة إدارة الإزالة النهائية (0222) ليوون يبي)**

**مقوم اتأسلرية**

06 نييلة عن حكومة بورلين افسلو، قدم ليوون يبي، بابعباره لوكللة الرئدة، تتحقا عن ليلتهلاك  
 للثيووفلوروكيبون في بورلين فسلو عن عام 0222 طبق اللقرر (54/45) د. وكلت لكجيرة للتقيد في توافق تقبي  
 اللتزام ها لكخصين في خطة إدارة الإزالة للهيبة لهورلين افسلو من أجل الإزالة لكامة ليلتهلاك  
 للثيووفلوروكيبون لحو ليل ايركل ورنلشلي 0222. وكان مجموع لكميل للبلغ 45 222 دولار أمويكي زلدا  
 لكلف دعم لوكلل للبلغ 422 0 دولار أمويكي ليوون يبي وبلغ 452 00 دولارا أمويكي ل حكومة ليلندا، قبتمت  
 لوافقة في لكجيرة للتقيد من ناحية للمبدأ وتم الإفراج عه الكل وكلكفي شويتجيني في اللتزام لكخصين  
 واللتزام لرباع وكخصين لكجيرة للتقيد.

**قدير لكجيرة**

02 بين لكجيرة عدم وجود ليلتهلاك من للثيووفلوروكيبون في بورلين فسلو في عام 0222 وأنظما ترخيص  
 للمواد للمبتعدة للأوزون في عمل جيد. ووجدت زيادة في ليلتهلاك ليدروفلوروكيبون - 0.4 و  
 ليدروفلوروكيبون - 0.00. وأقر للتقير أن بورلين فسلو ليلتهلاك ووقوع اللفقة في لكجيرة للمبتعدة

للأوزون، وهينايروكلون للثلي 0226 بنأف انقلون دون إقلي مي غطى الاتحاد اللقدى والاقص اديل غرب أف قبي ا بهورين افسلو وكوت فيوار وغلجي وطلاي والسغال وتوغو(،ي حظر الواردات ولإصدرات من جيع مواد طلفق انقل وباء و هاء والامعدات لتيت ضيها.

### تتقيقات الأملة

02 بلغت حكوم قبورلين افسلو عن ملت بهلا لخص فر من الامواد اللطى ووفلى ووروكبوية عملا بل مادة 2 من برتوكول نجنوري اللسنوات 0222 و 0222 و 0202.

02 بلغ الهيويب الأملة أن قلون الاتحاد اللقدى والاقص اديل غرب أف قبي ا لم ي عدل ب عدل حظر الامواد لبيدرولطى ووفلى ووروكبوية، ومع ذلك، ييسم ح لبي ا بترخي ص واردات من الامواد لبيدرولطى ووفلى ووروكبوية والامعدات لقطا مة لبيدرولطى ووفلى ووروكبون.

02 لاحظت الأملة أن تقير لتحقق اضوى توصية ببل ل لبقين لالحلي ثت أخذ في الاعتبار الامواد لبيدرولطى ووفلى ووروكبوية والامعدات لقطا مة لبيدرولطى ووفلى ووروكبون. وقدم الهيويب شرح اب أن مشروع لقلون لاجيد الامتخ دم ل حص سن ي بلبتداء من عام 020. ق دق دم لى لالحكوم ة لام فلقة لبي من ظرا لأن لبقين لالحلية لاوطية ودون الإقبي قلات طبق ل صدارتص راح لتقيراد لكون لبي سبه قيود لبي لبقدار الام موحه.

### توصية الأملة

00 قترغب اللجنة للتقبي في:

(أ) أن تسيط لعم ا ب لبقير عن لتتحق من ملت بهلاك اللطى ووفلى ووروكبون لهورين افسلو ولتمثال للبلد لالتمزام ا ب ازالة ملت بهلاك اللطى ووفلى ووروكبون؛

(ب) أن تسيط لعم ا مع لتقير بان بورلين افسلو قد بلغت عن ملت بهلاك صفر من الامواد اللطى ووفلى ووروكبوية عملا بل مادة 2 من برتوكول فوتريال في عام 0222.

كوتدي وبلقوري ر يتحقق من نصي ذ خطة إدارة الإزالة ن قاية ) 0222-0222 ( لايوري ب )

### تجيبه

00 نيبله عن حكومه كوت دى فوار، ق دم الهيويب، باعباره لوكله لارطه، تتحقا عن ملت بهلاك اللطى ووفلى ووروكبون في كوت فيوار عن عام 0222 وعام 0222 بطق اللقرر 54/45 د). وكن لت اللجنة للتقبي ذ ق د واقبت في اجماع هالربيع ولاخصين لبي خطة إدارة الإزالة لل لبي قكوت لى فوار من أجل الازال قاتامة لابت بهلاك اللطى ووفلى ووروكبون لبحول 0222. وكان مجموع لتمويل لبل ل غ 565 222 دولار أمريكي زط د لتك لبي ف دعم لوكله لبل ل غ 662 6. دولار أمريكي للهيويب وبل ل غ 00 005 دولارا أمريكي للبيري دو، ق همت لهوافقة لبي ه اللجنة للتقبي في من اجمه لبعدا وتم الإفراج عن الكل وكنل في ش وينعير في اجماع الربيع ولاخصين والاجماع لثامن ولاخمين للجنة للتقبي في.

### تقير لتتحق

0. بين لتتحق أن كوتدي فوار قد ققت الأهداف لشل المهمة لخص ملت بهلاك الامواد لمتقبة للأوزون لبي لمتوى لوطني ل عام 0222. وكان ملت بهلاك الامواد لمتقبة للأوزون لبي لبي في عام 0222 قدار 02 طن ا من

قدرات لتفاد الأوزون بل قبل ان قبل الحد الأقصى لاس موح به للبالغ 44.0 طن من قدرات لتفاد الأوزون بناء على اتفاق مع اللجنة التنفيذية وفي عام 2022، وجد أن لتفاد المواد المتبقية للأوزون هو 52 طن من قدرات لتفاد الأوزون. ومع البلدان الأخرى في الإقليم فرعي، إصمدت حكومة كوت فيوار قبلون الاتحاد القدي والانص اديل غرب بلق فيا. ويعمل نظام لترخيص في اللبش كل جيد وتتوصل للهيئات الحكومية لاشراك قبل فية.

### تتبعات الأمل

04 بلغت حكومة كوت فيوار عن لتفاد للتوفل وروكيبون بمقايير 5.5 و 00 و 00 صفر طن من قدرات لتفاد الأوزون عملا بل مادة البروتوكول منقري اللسن وات 0222 و 0222 و 0222 و 0202 على التوالي.

05 لاحظت الأمل قفلوات لغير قيين للعيان لتبلغ عها عملا بل مادة ل2 عام 0222 و عام 0222 بوليانا عن لوار دانقير لتيق. وبلغ عن لتفاد للتوفل وروكيبون في عام 0222 على له 52 طن من قدرات لتفاد الأوزون فيقير لتتح قبل قبل ان قبل قدار 5.5. طن من قدرات لتفاد الأوزون بلغ عها عملا بل مادة 2، وفي عام 0222 كل لتللي ان 02 طن من قدرات لتفاد الأوزون بل قبل ان قبل قدار 00 طن من قدرات لتفاد الأوزون. وأخطر للويب الأمل أن لوحدة لوطية للأوزون لشارت لى أنقير لتتح قوي ضوي عي ان اتدققة وثقت على لتتحق منيانات لمادة لالتى قدمت فعلا. و قدمت حكومة كوت فيوار بمس اعدة للويب، خطبا رسميا لى أمله الأوزون في 05 مارس/آذار 2020 تطبببغير لتفاد ها من للتوفل وروكيبون لتبلغ عها عملا بل مادة 2 عن عامى 0222 و 0222.

### توصية الأمل

06 قهترب اللجنة التنفيذية:

(أ) أن تحاط بعم اقتير لتتحق من لتفاد للتوفل وروكيبون في كوت دى فوار ولتعال للبلد بالتزامات إزالة لتفاد للتوفل وروكيبون بناء على خطة إدارة الإزالة للهي قلة لة من عام 0222 لى عام 0222 وأن للبدل بلغ عن لتفاد للتوفل وروكيبون في عام 0202؛

(ب) أن تلاحظ طبب حكومة كوت دى فوار لى أمله الأوزون بتيغي بيانان لتفاد ها من للتوفل وروكيبون لتبلغ عها عملا بل مادة للسنين 0222 و 0222.

أن يسيروا: الخطة الوطنية للإزالة لتتحق من أدق لة 0222-0222 (الهي قدي)

### مخبة

02 وافقت اللجنة التنفيذية في اجتماع الارباع ورائع عين على الخطة الوطنية للإزالة لأدقيا مع للويب كوكلة بتيق رة والي ريدو وللك لدلي كوكلة بتيق بتيق بتيق للإزالة لة لة في لتخدام للمواد للتوفل وروكيبون وربع اللويب والتوفل فورم اللقي قبل لى اير لكون لللي 0222. وجمعت الخطة لوطية للإزالة لأدقيا لعي من خطط طاعية لمكرة وأشطة جيدة ولتخدم لتتحق من اللتفاد على لمتوى لوطى. ولتغ الأموال للوافق على لاشطة الخطة الوطنية للإزالة قسي ستشراىح من الاجماع لاسباع ولتتلي لى الاجماع الارباع ولخصين بلغ 02 645 522 دولارا أمريكيا زطدلتك لليف دعم لوكلة للبالغة 0 254 220 دولار أمريكي.

## تقرير التحقيق

02 بين التحقيق، الهدف من شريفي قديموز إلى أغسطس/آب 2022، أن تدور في تحقيق الأهداف المنشأة من قبل هيئات المهلك للمواد المتبقية للأوزون في الامتثال للمادة 222 و 2022 مع المتبقيات في المواد المتبقية للأوزون يبلغ 020.56 طن من قدرات لتفاد الأوزون وحتى قدار 0... طن من قدرات لتفاد الأوزون في عامي 2022 و 2022 في التوليد. وتمتددة أهداف المهلك للمواد المتبقية للأوزون لجميع القطاعات (المرغوي وخدمة أجهزته في المزارات وتصنيع للتبريد وخدمته للتبريد والأيربوسول والمنتجات) في عام 2022 لجميع القطاعات ببلثان قطاع تنجيف مواء للمزارات في عام 2022. وتم الإبلاغ أيضاً في أن للميلية والإجراءات المتخذة وأعمال زيادة الوعي للمتحققين قاطعتهم بشرك في ق.

## تفويقات الأمل

02 بعدما ولقت اللجنة التنفيذية في آخر شريحة خطة لوطية للإزالة لأدوية في وقت ذلك في شرط أن يوصل لليونيهي، باعتبارها الوكالة الرائدة في إزالة عن الحكومة، تقديراً لسياسة تحقيق عن المهلك للثيوفولوروكيبون للمدة المتبقية من الثلاث، أي، لتتغنى لسنوات حتى 2020. وملتزم في تحقيق عن عامي 2022 و 2020 مفعلة؛ وكذلك قاري في تنفيذ لسنوات 2022 و 2022 و 2020. وتلار لليونيهي إلى أن تدور في حظرت لواردات من للمواد للثيوفولوروكيبون وربطه للثيوفولوروكيبون واليوسفورم الهميل والطلون بتداء من (ينظر في الملحق 2)، قبل جدول بروتوكول فيريال وأن للتحقق في هذا عام 2022 كذا الملحق للثيوفولوروكيبون. وتدير لليانات التي تحتها تدور في عمال للمادة 2 من بروتوكول زيميريال إلى المهلك صفر من للمواد المتبقية للأوزون) غير للمواد للثيوفولوروكيبون (للسنوات 2022 و 2020. وتلار لليونيهي إلى عدم في بذات جوهية خلال عامي 2022 و 2020 ببلثان للبرصد وأن الميزانية المتبقية للبالغة 06 222 دولار أمريكي يتم برمجتها لالتهاء من الأشظفي عام 2020.

2. تلار الأمل إلى حقيقة أن للتحقق في تحقيق المهلك للثيوفولوروكيبون عام 2022، في أنه بعد أو أقل من 0... طن من قدرات لتفاد الأوزون، في مختلف التبعيات التي انبجيات لجمارك مهفر طن من قدرات لتفاد الأوزون (ولم في موات من وزارة لتجارتهم) من قدرات لتفاد الأوزون (ولم في موات من المختب الاحصاءات) 0... طن من قدرات لتفاد الأوزون. ووضع لتبعيات من المختب الاحصاءات في أساس كل من سجلات لجمارك للمختبة والإلكترونية التي قدمها 02 موظف لجمارك. ونظر للتحقق وحدد أن لتلار في دوله اتج عن السجلات للمختبة لتقديم. ولتتغنى الأمل لليونيهي إلى أن حكومة تدور في اقتدبلت عن المهلك صفر من للمواد للثيوفولوروكيبون عمال للمادة 2 لعام 2022، وطهتوضيحا. وشرح لليونيهي أن للتحقق، بعد لتتغنى في مقارن من عدد من المصادر، حدد قدار 0... طن من قدرات لتفاد الأوزون من الواردات في بيانات للمختب المركزي للاحصاءات في تدور في تعيين ما لتوجد واردات في صدي لتبعيات أخرى؛ ومع ذلك، طب من الحكومة أن تتخذ في حل لتلار في انبجيات لتبعيات لجمارك لأن ذلك لتتغنى في يمكن الاعتماد في، بجنة المهلك صفر، ول هذا لتتغنى في للمادة 2 كملتم الإبلاغ في.

0. يؤكد للتحقق أن تدور في قد لتتغنى في الحكومة وللجنة التنفيذية بشأن إزالة للمواد للثيوفولوروكيبون في تدور في، وأن المهلك للثيوفولوروكيبون عامي 2022 و 2022 كان أقل من لحد الأقصى للمهلك للمادة 2.





## تفويضات الأملّة

5. بلّغت تغيير غيّن تان عن بلّغته بلّغته من المواد للثلاثين والستين من عام 2002 عملاً بالمادة 2 من بروتوكول جنيف. ويخبره بروتوكول جنيف الأول 2000 تم صرف جميع الأموال للوفاء بخطط إدارة الإزالة التي هيّئة.

6. في الاجتماع الثالث والستين، لاحظت الأملّة أن التقييم النهائي للمرحلة الأولى لخطط إدارة إزالة المواد للثلاثين والستين من عام 2002 هي ضمن تمويل معدات وأدوات إضافية لا يتعدى 52 في المائة من إجمالي قدرة أسبوعية (إعادة التدوير) الوثيقة UNEP/OzL.Pro/ExCom/63/37. وردا على سؤال من الأملّة بشأن ما إذا كانت الأنشطة البيئية العامة 2002 و 2000 في سياق خطة إدارة الإزالة التي هيّئة قد سمحت للحلّة، وأجاب ليوي بـ "نعم" أن معظم المعدات التي تمّ شراءها، بلشأنها لم تتراكم في آخر جولة من التقييم وانتبها على خطة إدارة الإزالة التي هيّئة، لمبحت الآن في حالة مقارنة بالأدوات التي تمّ استخدامها الآن. وبلّغت الوكالات المهذبة أن بعض المراكز سيجرى تحديثها كجزء من خطة إدارة إزالة المواد للثلاثين والستين؛ من غير المضمحل ليوا أن يكون تمويل الخطة في الاتفاق مع جميع المراكز.

2. قدم ليوي بـ بعض التوضيحات بشأن مقايير للثلاثين والستين من عام 2000 للمبتدئة والمعادتدوير هافي قرغستان (نظر إلى جدول 0). ومن مجموع 22 مليون غرام من المواد للثلاثين والستين من عام 2000 الذي تمّ بلّغه هافي قرغستان تمّ بلّغه وإعادة تدوير هافي مركز تركمت من عام 2002 إلى عام 2000.

جدول 1: مقايير ل مواد للثلاثين والستين من عام 2000 للمبتدئة والمعادتدوير هافي قرغستان

السنة	للمبتدئة والمعادتدوير هافي قرغستان (مباشرة في الموقع) (مليون غرام)	للمعادتدوير هافي قرغستان وإعادة تدوير (مليون غرام)	مراكز
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	

2. كُنتت الوحدة الوطنية للأوزون في قرغستان لوجود 5 وحدات للتدوير وإعادة التدوير التي هيّئة. هيّئة لثلاث وحدات تمّ شراءها في عام 2002 من خلال أنشطة خطة إدارة سويل للثلاثين والستين، أنتجت تدوير المواد للثلاثين والستين فقط، بين ما الوجودات الأخرتان، التي تمّ شراءها خلال تنفيذ خطة إدارة الإزالة التي هيّئة، هيّئة هم إعادة تدوير المواد للثلاثين والستين والمواد التي تدويرها في خطة إدارة الإزالة التي هيّئة. ولاي جرى إعادة تدوير المواد التي تدويرها في قرغستان نتيجة الانتقال إلى حافز بسبب أن تكاليف المواد الأولية التي تدويرها في قرغستان-00 مازالت منخفضة جدا.







للثيووفل ووروكيبون، ولتتحتاج الى التهاء فيها لأن هؤلاء للشركاء هم فبس للشركاء في إزالة ليدروفل ووروكيبون.

50 اقترحت الأمل، لئىضوء للتوري لقديم، أن خطة ل عمل الراق في لمن أنتغطى لالتزامات لهورى لمددة 00ش مرالقادحقق ط ولكن بطلغ قبل من لقترحي لجدول 0 أعلاه بم في ذلك لتمول ل لمطوب أشر رجعي. ولتترعت لتبناه لهورى ب ليطض اللى تحقيق أن للملا تربي جي طاش المثل خطة إدارة إزالة ليدروفل ووروكيبون لثيوين مازلت مبقية وليغت أن حكومة لثيوين يهبحي أنتسار عبالتهاء فيها مع الأخقي الاقهار الأموال لتبقي من لخطة لوطنية للإزالة ولانظر بشركل جدى في لثيوين فتكامل مذهبي خطة إدارة إزالة ليدروفل ووروكيبون خص لقطاع لخدمة. في لمن لظرفي صرف لرضيد لتبقي عرد مفلقة للجنة لتبقي في لئى خطة ل عمل لثيوين لتبقي في لمتقبل. وقدمت حكومة لثيوين ولهورى مي زلية بقى حل مدة 00ش مرالقاد تم لها لتوفى لجدول. لأناه.

لجدول 2: خطة ل عمل وليؤاني ل موفلق لئى هم لثيوين قمن رأيل/نيسان 2010 وائل/نيسان 0212

للمؤاني ل دولار الأمريكي)	بلي/نيسان 0210 بلي/نيسان 0212
65,000	فزع امداد اضرفي مل المواد المصنفة للأوزون بملدي ذلك لثيوين ووروكيبون ووروكيبون
170,000	ومصلة ل عمل في قطاع لخدمة (فزع الطلب على الكل ووروكيبون بم في ذلك لثيوين ووروكيبون)
30,000	إدارا ل مواد المصنفة للأوزون غير لطلوبة
20,000	الوعى فشر ل عمل ومات
143,550	وحدة ووكول متهريال
428,550	لم مجموع لرعى
43,080	التحويك بأر جعي (يولي قتموز 0200 ييس بركانون الأول 0200)
471,630	لم مجموع

### توصية الأمل

50 قترغب للجنة لتبقي في أن تتظفي:

(أ) أن تحاط لئى ما:

0(بتقير لتحقق ل عام 0222 ولت بهلاك للثيو ووروكيبون ل عام 0202 في لثيوين ولتمثال لليلد لالتزام بإزالة لت بهلاك للثيو ووروكيبون؛

0(بأن لثيوين بللغ عن لت بهلاك لصف من ل مواد للثيو ووروكيبون ل عمال بال مادة 2 من بروتوكول نهورى ل عام 0202؛

(بأن خطة لتبقي لثيوين ببناء لئى لخطة لوطنية لإزالة للثيو ووروكيبون لثيوين بئى لئى سان 0200 لئى بيل لئى سان 020. لتتقيدم هالهورى سبيلة عن حكومة لثيوين ولوافق لئى الأمانة الواردة في ملصرف ما لئى تجاوز بللغ 420 6.2 دولارا أم لئى ل مفضلت تروتط ب لئى لهورى ب أن يوقدم تقيرا سنويا لئى للجنة لتبقي في قبش أن لتقدم لتحقق لئى الاجتماعى لئى ببالشركل لتتسق مع ملئى ج عن لئى أقتش قحت لليلد 2)د( من جدول الأعمال؛

ب) أنت طلب من حكومة لليبيين من خلال الليوي بستيقيم خطة عمل سنوية لائحة للرصد للتحقيق للبالغ 0 422 000 دولاراً أمريكيي بما يثبت تجاوز الأخطار والتهديدات من الأخطار مع الأخقي الاعتبار الأموال للتحقيق إذ تم للظرفين أنشطتيسر إزالة للمواد الليدرولكي ووفلوروكبوي قيسي اق خطة إدارة إزالة لليدرولكي ووفلوروكبون للهد.

س او تسوي وبرنرهي يتقري للتحقق من تفنيذ خطة إدارة الإزالة النهاي ة (0222-0222) (ليوي ب)

### مخبة

5. نيبة عن حكومة س او تومي وبرنرهيي، قدم لليوي ب، بملعباره للوكالة للرطدة، تتحقا عن لمتهلاك للكي ووفلوروكبون في س او تومي وبرنرهيي من عام 0222 لى عام 0222 طبق للمقرر (54/45) د). وكلت للوحة للقيذي قد خلقت في اجامع هالربيع وللخمين عوى خطة إدارة الإزالة للني لس او تومي وبرنرهيي من أجل الازل في التامة لانتهلاك للكي ووفلوروكبون ب لحو ل 0222. وكان مجموع للتمهي للبالغ 022 222 دولار أمريكي زطد لتكليف دعم للوكالة للبالغ 2 252 دولاراً أمريكيي لليوي ب وبلغ 2.5 02 دولاراً أمريكيي لليوي ب، قدمت لوافقة للي ه للوحة للقيذي من ناحية التمهذ وتم الإفراج ع هالوكالة لني ش وي عني في الاجامع للربيع وللخمين والاجامع لربيع وللخمين للوحة للقيذي.

### تقري للتحقق

54. بين للتحقق أن س او تومي وبرنرهيي لبي هانظام ترخي صرفعال ووحدة وطيبة للأوزون قيية. وتتقت الأمداف لاش الهة لانتهلاك للمواد المبتعدة للأوزون عوى الامتوى للوطنى ل عامى 0222 و0222. وكان الانتهلاك لليوي من للمواد المبتعدة للأوزون في عام 0222 هو 2.0 طن من قدرات لنتفاد الأوزون) بلقارن بقدار 2.2 طن من قدرات لنتفاد الأوزون للحد الأقصى لاشتهلاك لاس موحب مناء عوى للفاق (ص فر في عام 0222) بلقارن بقدار 2.2 طن في قدرات لنتفاد الأوزون للحد الأقصى لاشتهلاك لاس موحب مناء عوى للفاق).

### تفويقات الأمل ة

55. بللغت حكومة س او تومي وبرنرهيي عن 2.0 طن من قدرات لنتفاد الأوزون من لمتهلاك للكي ووفلوروكبون عماللمادة 2 من برتوكول لنتري الفسي عام 0222 وبلتتهلاك صفر ل عامى 0222 و0202. يوطبق نظام للترخي ص ولا حصص في س او تومي وبرنرهيي عوى موادكل من للرفق ألف وللرفق ميم. ويجرى لصدار للحصص للبرني ل هه للمواهب اللشترك مع وزارتي للهيئة وللجارة.

### توصية الأمل ة

56. قهرغب للوحة للقيذي:

أ) أنت حاط عى ملتبقي للتحقق من لمتهلاك للكي ووفلوروكبون في س او تومي وبرنرهيي في لفترة من عام 0222 لى عام 0222 ولتمثال لليكي ليلتزامات إزالة لمتهلاك للكي ووفلوروكبون؛

ب) أنت حاط عى ما يضا بأن س او تومي وبرنرهيي بللغت عن لمتهلاك صفر من للمواد للكي ووفلوروكبوي عماللمادة 2 من برتوكول لنتري الل عامى 0222-0202.

## تقاي خـطـط الإزـالـة لـقـطـع طـحـيـة

52 قـدم الـيـونـيـيـي ولـنـك الـدولـيـي لـقـاريـر الـتـالـيـة:

(أ) (طـحـيـيـن: إزـالـة لـمـواد الـمـتـقـدـة لـلـأوزون فـي قـطـاع الـمـفـيـطـيـي طـحـيـيـن) عـام 2020 قـتـريـر مـرـحـيـي  
وعـامـي 0222 و 2020 تـحـقـق مـن الـأداء وعـام 0202 لـتـحـقـق لـلـقـنـى مـن لـقـو فـورم الـهـيـيـل  
(الـيـونـيـيـي)  
(ب) (لـقـنـيـيـي عـن تـقـيـيـذ إزـالـة رـبـع لـقـو رـيـد الـكـبـون لـقـطـاع الـمـفـيـطـيـي الـمـتـهـلـك و الـإـتـاج خـلال عـام 0202 لـنـك  
لـدولـيـي)

طـحـيـيـن: إزـالـة الـمـواد الـمـتـقـدـة لـلـأوزون فـي قـطـاع الـمـفـيـطـيـي لـلـصـريـن) عـام 2012 قـريـر مـرـحـيـي وعـامـي 0222 و  
0212 تـحـقـق مـن الـأداء وعـام 0212 لـتـحـقـق لـلـقـنـى مـن لـقـو فـورم الـهـيـيـل (لـيـونـيـيـي)

52 نـيـهـة عـن حـكـومـة طـحـيـيـن، قـدم الـيـونـيـيـي بـلـعـبـارـه لـو كـلـة لـقـنـيـي قـاريـر مـرـحـيـي قـسـمـي قـطـاعـي 0222 و 0202  
لـخـطـة قـطـاع الـمـفـيـطـيـي لـإزـالـة الـمـواد الـمـتـقـدـة لـلـأوزون فـي طـحـيـيـن و كـنـك لـتـحـقـق مـن الـمـتـهـلـك فـي مـتـخـدـامـات  
لـقـو فـورم الـهـيـيـل لـخـضـع لـلـقـبـل قـطـاعـي 0222 و 0202 تـحـقـق لـلـقـنـى مـن الـإزـالـة فـي عـنـة مـن ثـلـاث شـركـات مـتـقـيـدـة  
لـكـي تـظـنـر فـي هـا لـخـجـة لـتـقـيـيـي فـي اـجـمـاع هـل سـادس و الـتـيـيـن.

### تـجـيـة

52 و افـقـت لـلـخـجـة لـتـقـيـيـي فـي اـجـمـاع هـا التـلـيـيـن عـنـي خـطـة قـطـاع الـمـفـيـطـيـي طـحـيـيـن بـمـجـمـوعـتـهـا قـتـبـلـغ 50  
لـيـون دـولـار أـمـريـكـي زـطـد لـتـكـالـيـف لـدـعـم الـيـونـيـيـي. و تمـت لـهـو افـقـة عـنـي الأـمـو الفـي 00 شـرـيـحـة سـنـيـة لـتـقـيـيـي خـلال  
الـسـنـوات مـن 0222 لـى 0202، مـع الـمـفـلـقـة عـنـي لـشـرـيـحـة لـنـي عـنـي فـي الـاجـمـاع لـتـسـلـع و الـخـمـيـن.

62 تـحـقـقـت الـإزـالـة مـن خـلال الـجـمـعـيـيـن نـأشـطـة مـتـقـدـمـيـي قـتـسـت مـد فـشـركـات مـحـد دـقـبـر نـا مـج مـسـاعـدـة تـقـريـة  
لـشـركـات صـغـيـر قـتـدار مـن خـلال نـظـام الـسـنـدات. و تمـت لـفـصـاظ عـنـي حـدود الـمـتـهـلـك مـن خـلال نـظـام الـإـتـاج و الـو اردات.  
و تـجـرى لـو قـبـلـة عـنـي قـصـص الـإـتـاج مـن عـنـي خـطـط الـإزـالـة فـي قـطـاع الـإـتـاج لـلـمـواد لـلـقـو فـلـو رـكـبـيـة و رـبـع  
لـقـو رـيـد الـكـبـون. و تمـ حـظـر مـتـخـدـام رـبـع لـقـو رـيـد الـكـبـون كـمـفـيـب مـن 0 يـو مـيـة/ حـفـيـر ان. 022، و  
لـلـقـو فـلـو رـكـبـون. 00 كـمـفـيـب مـن 0 يـو مـيـر لـكـل و رـكـل مـثـلـي 0226؛ بـونـاء عـنـي لـكـتـم الـقـتـهـاء مـن الـأشـطـة ذات  
لـعـلا قـتـيـي الـسـنـوات لـمـضـيـة. و تمـ الـقـتـهـاء مـن إزـالـة مـتـخـدـام لـقـو فـورم الـهـيـيـل بـاعـبـارـه آخـر مـفـيـب مـن الـمـواد  
لـمـتـقـدـة لـلـأوزون لـذـي و يـتـيـت حـت هـذـه الـخـطـة طـحـيـيـن بـمـجـمـوعـتـهـا لـقـو رـيـد الـكـبـون مـثـلـي 0202.

### الإزـالـة مـن الـمـشـرـوعـات و الـأشـطـة الـمـتـقـدـمـيـي

#### الـأشـطـة عـنـي مـتـوـى لـشـركـات

60 بـنـاء عـنـي خـطـة قـطـاع الـمـفـيـطـيـي مـتـحـقـق لـقـصـص الـمـسـجـل فـي عـام 0202 بـلـسـطـة الـقـتـهـاء مـن نـأشـطـة الـإزـالـة فـي  
لـشـركـات سـنـبـاء عـنـي مـشـرـوعـات عـنـي مـشـرـوعـات مـتـقـدـمـيـي لـلـأوزون لـتـيـبـدأ تـقـيـي عـامـي 0222 و 0222 لـإزـالـة  
لـقـو فـورم الـهـيـيـل لـمـتـخـدـم كـمـفـيـب. و مـد عـام 0222 تـقـيـي نـأشـطـة مـجـمـوعـتـهـا قـصـص قـداره 2.2 طن مـن قـدـرات  
مـتـقـدـمـيـي الـأوزون مـن لـقـو فـورم الـهـيـيـل، و عـام 0202 قـدار 2.2 طن مـن قـدـرات مـتـقـدـمـيـي الـأوزون مـضـافـي.  
و بـالـمـجـمـل، أزـالـت خـطـة قـطـاع الـمـفـيـطـيـي 042.22 طن مـن قـدـرات مـتـقـدـمـيـي الـأوزون مـن مـتـهـلـك لـقـو فـورم الـهـيـيـل  
تـحـقـقـت طـوال 00 عـام و فـي الـسـنـوات الـمـتـبـاق قـتـج عـن إـحـلال الـلـقـو فـلـو رـكـبـون. 00 قـصـص مـجـمـوعـلـغ 0622.5





و 0202 . وتم تنفيذ التمويل للتقني خلال عام 0202 من متويبدلبلغ 6 204 602 دولاراً أمريكيين هبة عام 0222 بمشمل حيت ترك إرصدفي حس ابلل مشروع.

### تتويقات الأمل ة

66 وافق الاجتماع لتلوع والخمسون فيوفم بتشيزنل لثلي 0222، توي عدد من الأشطقي ضطعبها بالأموال للتقني في ذلك الوقتكثير من 2 ميلايين دولار امويكي و في عام 0202، قام اليونانيون هبة عن حكومة طين مبتويشلك الأشطة لولتزم بأموال لمشروع للتقني ة.

62 إنقويم اليوناني هبة عن حكومة طين زوفر نطرة عامة مجازة وفصلي ة للأشططيناء توي هذه لخط ة، نولك ائح للتقني ذلك من عام 0222 و عام 0202 وللك منب طية لخط ة. إن تويقات للتقني لقدم تل عامي 0222 و 2020 لتقني وفير للقة الكالت في ص ح ل ام توي مات لقدم ة. إن تويذ خط ة قطاع ل م فلت قد ت مت.

### توصية الأمل ة

62 قترغب ل لجة للتقني في:

(أ) انتحاط توي ابلل تقير لمر لحي لفمترة 0202/0222 لخط ة قطاع للصبات لإزالة ل مواد ل متفدة للأوزون في الصرين؛

(ب) أنتحاط توي تقارير للتقني من ل توي وفورم ل هبيل ل ص ابلل عامي 0222 و 0202.

الهن تقري زني ذ خط ة إزالة هك لوري نال لوب و في قطاعي اللات هلاك ولاتاج خلال عام 0212 لبلنك الدولي )

62 قديم لبلنك الدولي باعبار ه لولك لة ل هبة، لى الاجتماع ل خامس ولتيني ن هبة عن حكومة ل قدم تقني من لجات لبلون امج للزن و ل عام 0202 و في سباق هذا التقويم، لاحظت ل لجة للتقني في ق رر ه 02/65 (أ في للتقني ق ت متصريف لتخدام ربلع ل توي ربلع ل كيون لإنتاج ل توي ل هبيل الأحادي توي له مواد أولية منب طية عام 0225 ميين طي عام 0222 ت متصريف لتخدام ربلع ل توي ربلع ل كيون في إنتاج ل توي ل هبيل الأحادي ك عام لتصريف ل هبيل من قبل الاجتماع لولتس ع عشر ل لأطراف في بروتوكول ن جتري ال ) ل ق رر 15/XIX . و طبت ل لجة للتقني في أيضاً لى بلنك ل دولي في ل ق رر ل طر عة ) . ( من ل ق رر أن تطب من حكومة ل ق ت ح هبتي انات لت هلاك ربلع ل توي ربلع ل كيون من عام 0222 لى عام 0202 ل ل طغ ع ه لى أمل ة الأوزون عملا بل مادة 2 من بروتوكول ن جتري ال . و طبت ل ق رر ل طر عة ) 4 ( من فس ل ق رر لى بلنك ل دولي للتقني ق مع حكومة ل ق ت ح حري عن أي مدي دمرت لعميات ربلع ل توي ربلع ل كيون في الأعوام 0222 و 0222 و 0202 لتعوض لعميات ربلع ل توي ربلع ل كيون ل م ت خدمة ك عام لتصريف ل هبيل لإنتاج ل توي ل هبيل الأحادي في الأعوام 0222 و 0222 و 0202 وأن تق هتقري را تقني لبلنك لجات اوز 2 ل بلع قبل الاجتماع ل س ادس ولتيني .

22 وفي أعقاب الاجتماع ل خامس ولتيني ن اقش مؤتمر الأطراف لثلاث الو عشرون مس لة ربلع ل توي ربلع ل كيون ل ل تخدام ه ك عام لتصريف ل هبيل ي بشلك ل عام و في ل توي ل هبيل الأحادي بشلك ل خاص . و نص ل ق رر ) 2 ( من ل ق رر 7/XXIII "ل لتخدام ل مواد ل خض عة للوقيلة ك عوام لتصريف ل هبيل ي ية" أن الأطراف ل تظرفي لتخدام ربلع ل توي ربلع ل كيون لإنتاج ل توي ل هبيل الأحادي لأغراض ل متوي ات ل م ح رة ل إنتاج واللات هلاك، توي اساس لتقني، ل لتخدام ه ك مادة أولية ضي 0 ممبر لكون لثلي 0200" . و ت عبر ل ق رر وارد ل لكر أن ل ق ررين ل طر عين ) . ( من ل ق رر 02/65 ) ل لجة للتقني في غير ذ ل ت.

20 طب لقرار 02/65)ى(5) لى بلنك لدولي أن يقترح ريش أن تفيذ خطة إزالة رباع لثوريدي للكربون في قطاعي الإنتاج والبناء هلاك خلال عام 2020 في وقت إل قرار الاجتماع لسادس والستين، وإذا لطبق، فتقترح الأنشطة لامخطة وأقر لتقرير لذي قدم بلنك لدولي أن لامراجعة لتقريره لتتحقق من إنتاج ولبت هلاك رباع لثوريدي للكربون لعام 2020 تم الاضطلاع به في مارس/آذار 2020. ولبت خدم بلنك لتفريق مراجعة لم نقل لتقرير امارات للهواوع ولبت عرض وثائق أبعه فتعنين لرباع لثوريدي للكربون وتطوية فتعنين ل- dichloro vinyl acid (DVAC) chloride (DBBP) di-fluro benzophenone (DBBP) واحدل- وثلث ريش أنت خزني في هواء كندلا وبالباب ل عام 2020، لم تصدر لجهة الأوزون حصص للبيع لكلمت خديين من غير للمادة الأولية. وكفريق لامراجعة عدم وجود بيعات متباشرة لميت خديين من غير للمادة الأولية لم يتيم لتقريراد أوتصديري رباع لثوريدي للكربون من قبل فتجى رباع لثوريدي للكربون. ول هذات فتقريوق لامراجعة لم نقل أنفي ربه أن لافهت تتحمل لتزامات تبروت وكول لتقريرال. وكان آخر صرف من الأموال من خطة إزالة رباع لثوريدي للكربون) 0.0 لليون دولار أمريكي (لأبعه فتعنين لرباع لثوريدي للكربون في سمبر لثون الأول 2020 وفي عام 2020، لم طاعت لالجهة لوطية للأوزون بعدد من لتقات ل العمل وأنشطة لتدي ببناء هوى لمون لامساعدة لتقريره.

20 بلل غلنك لدولي الأمله أن الأموال لتتجيه للهالغة 0.4 لليون دولار أمريكي يتم لإلتراح أنت غطى بتديري مجموعات للصناعة ولربط لميت خديين لرباع لثوريدي للكربون لل عمل مع بتل للهيئات) 222 422 دولار أمريكي؛ وض عدلات ربيحية للاصصالات وتفيذها لتتجرب لميت خدام رباع لثوريدي للكربون ولتبع للميت خديين من الإلتداد) 222 022 دولار أمريكي (تديري لالحكومات لاملحبة وموطني لمجلس كلفحة للثوث) 222 026 دولار أمريكي؛ لتقات لتديري لموطني لاجمارك) 222 026 دولار أمريكي؛ لم دارق صصن جاج) 222 2. دولار أمريكي؛ الأنشطة وح دتبروت وكول لتقريرال لاجارية بم في ذلك لارصد) 222 022 دولار أمريكي. وتشارت الأمله لى فتقوة أن رباع لثوريدي للكربون في الإلتخدامات لالخصع للوقبة فتتم إزالها فتكث من عام. وتشارت ق لخطي حول لكرية ازواج لتهم لبل قارن قبال أنشطة لسبق ببناء هوى خط لقطاع وللك مع تديري لاجمارك لمطوب أصاب بناء هوى خطة إدارة إزالة لايديرو لثو ولفلوروكيون لك قدي لتي قدمت لى الاجتماع لسادس والستين. وتشارت الأمله لىض امس لمت لتقريب لخطوط لتتوقع الأنشطة ممتفق قدمت عددا من لتتبرحات مشمل اضا فت أنشطة لارصد ما إذا كان رباع لثوريدي للكربون لكلمت لتعمل غير للمادة الأولية فتتحت حوله لى لميت خدامات خضع للوقبة، وتحويل الأموال لى أنشطة أخرى لتل أنشطة خطة إدارة إزالة لايديرو لثو ولفلوروكيون.

2. قرر بلنك لدولي فيبيلة عن حكومة لوقد، سحب لتقري من ظرا لأن اللاتقيات للمخطة لتتخري صتمويل يتطوبق لتكثرت للظن. إلا أن الأمله اعتقدت أن من الضروري أن يقيم هذا لى اللجنة لتقوية عمال لقرار 2/0. لاجتماع الأطراف ولقرار لقرار 02/65)ى(5) لذي يتتقير الى الاجتماع لسادس والستين.

24 قهترغب للجنة لتقوي في أنتنظر:

أ) (في الاحاطة لم لمب أن لقورة 2 من لقرار 7/XXIII من الاجتماع لثلاث وتشريرين لاطراف لذي يتتبر لميت خدام رباع لثوريدي للكربون لتتاج لتوريد لتيول الأحادى لغرض لميتويات لم حبوب لتتاج والبناء هلاك، هوى اساس لميتنظري، لكون لميت خدامه كم مادة أوية صى 0.0 يتصبر لثون الأول 2020، تبطل لتقويين لتريين). (و) 4) من لقرار 02/65)ى(للجنة لتقوية؛

ب) أنتطب لى بلنك لدولي أن يقيم لى الاجتماع لتتسرع ولتتقير الى عن حلة لميت خدام رباع لثوريدي للكربون في قطاع لتوريد لتيول الأحادى في لوقد؛









## خامسا مشروع تدمير المواد المتفجرة للأوزون

20 طبل مقرران (02/52 أ). (و 52/64 لى لوكالات للتقييم والقيادة الإلغ للنويفي أول اجتماع للجنة التقييمية عن لتقديم المحرز والخدمة المتسبة من مشروعات لتدمير للتخلص من المواد المتفجرة للأوزون بدأ من أول اجتماع للمفلة عنى للمشروع، وأنشئ ملفي هذه للتقرير مقومات عن: مقايير للمواد المتفجرة للأوزون المتفجرة التى جمعت أوت حددت وقتها وتخزينها وتدميرها ولتقلل للتبقيات الحظية والإدارية ولتسهيل للتصترك وأي مسائل أخرى ذات علاقة. وقد تمتق اوير عنال مشروعات لاجاري لتدمير للمواد المتفجرة للأوزون فليكوبا وغلا لى الاجتماع لاسادس والتين بطق النهي المقرررين.

كوابتقير حالة عن مشروع بيئي بحري بي بشأن إدارق فليات المواد المتفجرة للأوزون فلتخلص من ها لاي عن بي

## نخبة

2. تمت لهوافة عنى مشروع بيئي تجريبى بشأن إدارة فليات للمواد المتفجرة للأوزون ولتخلص فها في الاجتماع للتلي والتين بملغ 505 022 دولار أموكي يثدمير ما مجموع ه 45 طن متري منفايات للمواد المتفجرة للأوزون، عنى ان يكون من الفهوم أن ملن يقدم في لاضافى لاطكوبا لأي مشروعات للتخلص من للمواد المتفجرة للأوزون في المقبل المقرر 02/60). هيس على مشروع لتجريبى لى وضع إطار لوجستى فعال لى فالتالي فلتقل للمواد المتفجرة للأوزون وتخزينها وتدميرها فليكوبا.

## لتقديم للمحرز

24 وقعت وثيقة لمشروع البيئي بليكوب لى بي بي/حزيران 0200 وتمن اش فمصري قال مشروع عمل مشاركة لكالمه لاجيى الأطراف لهوافة. وشمل لتقديم للمحرز: لاهول فيات للتقوية وتحديد للمعدات لمطوية لتلخيص رفقت تدمير للمواد المتفجرة للأوزون للمصار يهبلنء وتجيىع للموقفى عام 0200)ت تحيد للتطلبات والمعدات للتش فظية لرافق للتخزين لاج هية مختص يمشا حة بتخصص لاجمع للمواد المتفجرة للأوزون وقتها عنى ح الاطار لاقولني لضماتن فلي تدمير للمواد المتفجرة للأوزون.

25 لحتب معد لهه في لام هام فلي فلي ذلك جمع ولتدمير، ومعدل كتبت لتلج ارب بمجر د الاتهء من الإشاء الألى.

## تلتقيات الأملة

26 ضيى سم بركلون الأول 0200، لمحتب مصرف أي أموال نظرا لأن الأنشطة الألية لتى تتضم من تعديلات عنى رفقت لدميري جريت موهلها عنى ح وشبتر كمن قبل الحكومه للتويية.

22 يخرن لى قدار 0.2 طن متري من للمواد المتفجرة للأوزون في سبت و دعت تخزين ج هوى. وشار لى بي لى أن جيىع للمخزونات هى فضايات للمواد المتفجرة للأوزون ولاي ملن إع اة دويرها أو لى تصلادها.





الطاقة هي من المواد الخطرة ووكبونية، التي تمتحها هي ما تبقى لها بغيره كفايات للدمير عند المفارقة هي المشروع.

02. أخطر الهيون هي الأمل أن المشروع قد يبطله قبل أن يظن لأهية زيارة الانتشاري الدولي لغان في 0200 ليتم ادف معبيلة لخلق العمل لمشروع رفق للهيئة لعلها كفاءة الطاقة لضمان طرائق لتأزراتيين مشرعين فيفس للوقت وتآخر مذياري جة لتتويج الممتأخر هي وثيق لمشروع رفق للهيئة لعلها كفاءة الطاقة.

توصية الأمل

024 قترغب اللجنة للتقنية:

(أ) أنتحاط هي مقترير حالة مشروع يعل يت جري يش أن إذار كفايات المواد المنقبة للأوزون ولتخص في هالغان الذي قدمه الهيون هي؛

(ب) أنتطلب الى الهيون هي أن يقدم الى الاجتماع التسلع والبيين للجنة للتقنية فيمقرياً عن لتقديم لامحرز والتجربة المختبة من المشروع على لي لتجربيل غل ابطق لامقررين (02/52) (أ). (و 52/64).

**سادس: مشروع بئايه ومنتج ماري دل هي دوله وفلوربوربون**

025 قدم الهيون هي تقريين مرخبيين فيصيريين عن مشروعات ليدرو ولفلور ووكبون للتله:

(أ) علمي بتقري عن تقويم لبي للال كعلم في لتاجنظم رغاوى للبريوتان (الهيون هي)

(ب) علمي بتقري عن تقويم مخيرات لتكليف لفي خصصة لانتخدام ليدرو بون اتفي لتاج رغاوى للبريوتان (الهيون هي)

عليه: لام بي للال كعلم في لتاجنظم رغاوى والبلوي وبرتان بتقري ملتطيق في مشروعات لاصرف دوق المهمت عدد الأطراف

تجيبه

026 قدم الهيون هي الى الاجتماع لسادس والتين تقري لتقيا عن لبي للال كعلم في لتاجنظم رغاوى للبريوتان بتقويم لتطيق في مشروعات لاصرف دوق لتعدد الأطراف. ورفق بتقري لتقني الكامل (الاضافق لتقنية) ب هذه الوثيقة.

022 في اجتماع لثامن ولخمسين، وفاق لتجربة لتقنية هي مشروع تجريب لتحقق من لبي للال كعلم في لتاجنظم رغاوى للبريوتان، هي أن يكون من لفهوم أن معدات لتجرب لامتوية لتحقق من لتنولوجيا ستمنح الى رفق بوحت لا ييسر على لبوب حمررد التهاء من لمرطحين الأولى لولثية من لامشروع على لي المقرر (2/52).





عطي انتائج الاختبار لتغيير التوجيه حول ما إذا كانت الأوضاع التشغيلية للبخارية يمكن للتنبؤ بآثارها إضافة الرغوي؛ بتقني متغير لتكليف التشغيل الاضفلية بخي أساس للتعلج للتخفة؛ موصولة دراسات للتوازن المتقرر طويل الأجل خواص الرغوي، خاصة للتوازن المتقرر بلعدى؛ إدراج معدات رصدك لمكون تكامل لكل مشروع لضمان السلامة لتشغيلية ولشخصية.

### تقنيات الأملة

005 شمل مشروع التحسين لتقييم لثيلايل لخدمة عمل لنشرون تلج المشروع التي عرفت في البرازيل في ديسمبر كانون الأول 2000. وحضر أكثر من 022 شركاء في ذلك طحين عن: 00 كمتبتلن لوجي في البرازيل بملية لموكه ملجيا هي Amino, Arinos, Ariston, M.Cassab, Polisystem, Polyurethane, Purcom and Utech وأبعة لمعتب أنجبة هي Bayer, BASF, Dow and Huntsman. شرك قبتاج رغوي من البرازيل وجاطيكوت ريفي دلتوب اغو؛ خ من قبلدان من بلدان الامدة 5) أي، كلبويي وينا وأروغو اي بويرو وجاويكا)؛ لليونيهي وليريبي وألميا؛ وثلاث ريلطصرا نجي قبرا ليلية مثلية هنجين/هزعين لعوامل فخ من البرازيل وليجيك والوليات للخدمة الأمولية؛ 6 هنجين لمعدات حقن الرغوي؛ أبعة أعضاء لخدمة لخيارات لتقني لقل رغوي.

006 بوناء بخي طبتنصي حل معدات إعادة للتجهة و/أو معدات جي دقتطب جرد لتخدم تلن لوجي لثيلايل، شرح لليونيهي أن لثيلايل يمكن تقني هذه عامة دون تغيير للمعدات في خط الأساس وتتعلق لتكليف للبخارية الأساس لتطبات للعبودية لموزعات الرغوي وتركيبة قمي اس حس ليلية لثيلايل) أوبديلا عن لك، تخيمات مسح عافية للظافة للسناعية من قبل موردي للنظم) وعوادم الشعاث وتطبت معدات جي دقتطقي لالحالات حيث تقوم لمبتطل بإجراء الإرخاخيوي.

002 وردا بخي سؤال ما إذا كان أم لا فالكبراءات و/أو حقوق لملي قلكي قتشمل لتخدم لثيلايل كعامل فخ الرغوي، ثار لليونيهي لى وجوب براءات نعددة لمعض لتخدم لثيلايل. ومع لك، لاتوج ببراءة غطى بشرك ل شامل لتخدم لثيلايل كعامل فخ بخي رغوي للبوليوريثان، ولتوجد محاولات من قبل أي شركة أوليان أخرى دعي لملي لتلن لوجي لخدم لثيلايل) ومزال ليهي خدم قمي لاعي د من هنجي للاي لوي اتفي لتخدم لثيلايل بولوريثان بالاضافة لى بخي 2. شرك قمي أوب، ومن للصعب جدا ان يدعي أحد هذه لتلن لوجي يفرض ترخيصات. بل ماذفي رأي Lambiotte و Arinos ولليونيهي لى يمكن لتخدم لتلن لوجي ببحرية.

002 وسعتن اول جيع لتقنيات التي ثارات الأملة لاقطام بخي اللتعرض لتقني، قام لليونيهي بتقني حل لقيرو لن طائل مشروع علي لى متبع لك.

### تبصيرة الأملة

002 قهترغب للخدمة لتقني في:

(أ) أنتحاط بقم مع لتقير بالتقير لدمون " لثيلايل كعامل فخ في قبا جنظم رغوي للبوليوريثان. تقوي لمبتطيق في مشروعات للرن دوق للمعدد الأطراف" لذي قدمه لليونيهي؛

(ب) أنتطبل لى لوكالات للتقنية ولاهذه أنتقل بتقير بتقويم لليونيهي يش أن لثيلايل، مع الام لوجومات بش أن للخط، جرد من اعدة قبلدان للمادة كفي إعداد شروعات لإزالة لاي درولن ووفل وروك بون-040 بفي لتخدم لثيلايل رغوي للبوليوريثان.



لاي درولغو وفلو وركبون- 040 ب ك خ ط أس اس بين ما عشمس تايز مورات لبيتان فلأضريات السوق لالحلية. وتم تقييم ج جي عن نظم فخ لبيتان عوى ل أن انظم شركل قبل الكامل به مفيد ذلك عام ل لفخ (و باعتبار انظم م لخطوة جزيا) لضي ف عام ل لفخ لهدف قشلت).

**الجدول 2 نظم الفخ الدرغ اوي الم بخارة ل لا خبار**

عامل لفخ	تلبيد ل خارجي	الأواح غير ل تبصرة	س خقات ل ياه
فلي درولكو وفلو وركبون- 040 ب	النظام أ لف	النظام مجم	النظام هاء
الهيكل بيتان	النظام باء	النظام دال	النظام واو
البيتان ل عدى	النظام باء	النظام دال	

002 بتبين تلخج الاختبارات أن:

(أ) تم تلبيد لتوازن لفي لطي والليمي لطي لنظم لسيل لبيتان تحت أوضاع معيارية عوى 6 ش مر. أم انظم لبيتان ل عاي فلم تلقي متوازق أك ثر من ش مر واحد؛

(ب) بالنسبة للنظم ل م لخطوة مبقا، بحيث لا توجد حاج ل لنظام م ل خط سبلق، يتوق ع فور اتفسي لتكليف حول 022 222 دولار أمريكي؛

(ج) بالدرغ م من أن ل حقن ل لم بشر لا توجد فور اتفسي لتكليف ل معدات في مكن لتخصيم ل مدمج أن ل بيت ج وفورات في لتخ طي و لتخزين؛

(د) إذا كان من ل م مكن "ترجم تلك ل إضافة ل حرية ل فضضة للبحثا فتطويقية في فضضة، ي مكن يتوق ع فور ات في لتشغيل بين 6 و 2 في ل حلقة) أو 02 في ل حلقة مع ل حقن ل لم بشر (بالقارنة ببنظم لاي درولغو وفلو وركبون- 040 ب. ومع ذلك قهتني لتكليف ل لقل؛

(هـ) بين الانفعا لسري ل عمل - k بل بين 5 لى لفي ل حلقة) ولفعا ل ل فضض أن إبتظام رأس الم لخط قد ع لى من ليت خ س لم دفق شلت. و بين ما ي مكن أن ي ودى لتحسن مع مجموعة ل مزم مثلية لى إعاد تصيم م ل خط رأس ل موزع لى هذا من ك حاج ل لظن فيه.

002 بين ملتعب ج جي ع لى انات لتقوية ص ل حة علمي افيليني انات لتلغية هي ذات علاقتق ط م صر و ت خاج لى ت ع لى ما لأقل ميلدان أخرى. و بين ما لى و ن يبي حدد مجالات عيدة بحيث لتتبع ع مطوبة لفاءة راس ل لخط والبت خدام الأنامل ل م ل م (يبدو أن تلك اى ج ل ل حلقة م همة و تبرن ش رافورا.

**لبيتان ج ل ان ق د لتقوي**

002 لبيتان ل ل ا ق د لتقوي أن ل دربل ع ق ت ع ق ت من ل خواص فيزي لية ل قبل ل م ل حاجات ل درغ اوي الصر لية لتلبيد لتجاري والأواح غير ل تبصرة و لبت خدامات س خلات ل لى ا ب لبت خدام نظم ق ط مة عوى لاي درولغو وفلو وركبون الم ل خط ل ل ف و لتلك ل م ع ليرة ل لم بشر ل لى د ل و بونات؛ و ت ع ق ت من التوازن ل م ت ق ر ل نظم لسيل لبيتان ل م ل خط مبقا ل ل ليرة 5 ش مر؛ و تتوصل ل لدراسات لتحقق من ل حد الأنى بسبب لى م ل ر ل ج اة ل ل ر ف ب ق ب بين أن نظم n بيتان غير في لبة ل ل ل خط ل ل م ب ق ن ي ج ع د م ت زان (م ر ل جة ا ق ن ص ال) ل ل م ل خط مبقا. و بينت ل دربل ل م لبت خدام و ح د ت و ن ي ج ذات ثلثة ل مونات صر ل م م ت و ف ي ر ل م رة في ل ل م ي ا ت ب ي ن ل انظم ل م ل خطوة مبقا و نظم لاي درولغو وفلو وركبون ل م ع ليرة ل لم بشر ل.

للتوصل ل الحاري ل لوحة س م ك ل مادة.





ب) أن تطب لى الهيون هيبي الات هاء من لت تحقيقات الاضافي قبش أن المبرطل لتب نقي قبل س لامة وللخففات والابتخدام الأتمل للمعدات ووضع فم هوم للتكليف قوائم نغى بوليولات لاي دروكيون سبقة لالخط وقوي مقي رض افي لى الاجتام غاسبوع والسيتين؛

ج) أن تطب لى لوكالات تلكن بية والفيذة أن تتقبل مقترى رتقييم الهيون هيبي بش أن نيارات لتكليف لافقضة لابتخدام لاي دروكيون اتفي لتاج رغوى للولي وريشان، مع الم نغوم انتبش أن للبتل الأخرى، ندمس اع دقل دان لامادة نفي إعدام مشروعات لإزالة لاي درولن ووفل وروكيون- 040 بفي لتبخدامات رغوى للولي وريشان.

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
I.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
	<b>1.4 Training/Seminars/Workshops (local and international)</b>				
	1.4.1 Attendance to financial and administrative workshop to harmonize the policies of UNEP and the GoP	1	8,200	June 2012	
	1.4.2 Attendance to technical training to ensure the compatibility of Philippine system with China web-based system in tracking the stock of CFCs in the global market	1	19,048	3rd Quarter of 2012	
	1.4.3 Follow-up training of partner agencies and regional offices on database management and maintenance	4	28,571	3rd Quarter of 2012	10,000
	1.4.4 Regional forum on the updates of the NCPP Project Implementation and other NCPP implementation requirements	2	28,572	June 2012-April 2013	
	<b>1.5 Turn-over of training equipment to Training Institutes</b>	150 sets			
	1.5.1 Conduct meetings with TESDA on the findings of the assessment on the training equipment conducted by NCPP-PMU	12	286	Jan -June 2012	
	1.5.2 Conduct physical verification of training equipment nationwide	16 regions	11,905		
	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				
	1.5.4 Preparation of documentary requirements and distribution of deed of donations	150 Training Institutions & 16 EMB Regional Offices			
					5,000
	<b>1.7 Preparation of Project Completion Report of overall implementation of the NCPP (for the period 2012-2014)</b>				
	1.7.1 Hiring of Individual Consultant for the preparation of PCR	1	4,762	January-April 2013	
	1.7.2 Conduct of annual financial audit	2	4,762	2012-2013	
	1.7.3 Preparation/Finalization of reports (closing of books, meetings with partner agencies, TWG, etc.)	2	1,429	January-April 2013	
<b>Sub-total</b>			<b>194,169</b>		<b>143,550</b>

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

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

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
	<p>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:</p> <p>3.6.1 Conduct coordination meetings with LTO on the preparation of assessment report on the compliance of motor vehicles to refrigerant type</p> <p>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</p> <p>3.6.3 Conduct of MAC random roadside inspection by a composite team on a quarterly basis</p>	<p>10</p> <p>108</p> <p>80</p>	<p>1,190</p> <p>205,714</p> <p>9,524</p>	<p>2nd Quarter of 2012</p> <p>2012-April 2013</p>	<p>80,000</p> <p><b>170,000</b></p>
<b>Sub-total</b>					
4. Management of unwanted ODS	<p>4.1 Collection, transport and storage of recovered refrigerants from service shop grantees and chiller owners nationwide including confiscated refrigerants</p> <p>4.1.1 Conduct coordination meetings with DELSA on the CTS scheme to cover other regions</p> <p>4.1.2 Hauling of collected/confiscated refrigerants (from regional key areas to central CTS facility)</p>	<p>16 regions</p>	<p>72,857</p>	<p>2012-April 2013</p>	<p>30,000</p>
	<p><b>4.2 Procurement of additional Equipment for the collection, transport and storage of recovered refrigerants from service shops, chiller owners, etc.</b></p> <p>1. 10 units of 1 tonne tank/cylinder</p> <p>2. 4 units Recovery Machine</p> <p>3. 1 unit Transfer Pump</p> <p>4. 20 units (100 KG Cylinder)</p> <p>5. 1 unit Moisture meter for quality assurance for recoverable contaminated refrigerants</p>		<p>79,546</p>	<p>2nd Quarter of 2012</p>	
<b>Sub-total</b>			<b>152,403</b>		<b>30,000</b>

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	
	<b>5.3 Development and production of IEC materials</b> <ul style="list-style-type: none"> <li>- Amended CCO for ODS</li> <li>- Revised Code of Practice</li> <li>- Updated NCPP Primer including HCFC</li> <li>- Brochures and leaflets</li> <li>- Tarpaulins/Posters</li> <li>- Newsletters</li> <li>- Web Pages that highlight service shop beneficiaries</li> <li>- E-learning training modules</li> <li>- Social Networking</li> <li>- Video Documentary</li> </ul>		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	
<b>Sub-total</b>			<b>20,000</b>		<b>20,000</b>
<b>GRAND TOTAL</b>			<b>453,081</b>		<b>428,550</b>

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

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

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

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



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

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

### *Disbursement*

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

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

### *Organizational Structure*

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

### *Monitoring procedure*

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

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

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

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

#### *General Issues:*

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

#### *Disbursement*

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

#### *Organizational Structure*

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

#### *Monitoring procedure*

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

#### Meeting with UNDP, Pyongyang Office

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

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

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

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

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

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

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

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

### 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.



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**METHYLAL  
AS BLOWING AGENT IN THE  
MANUFACTURE OF  
POLYURETHANE FOAM SYSTEMS**

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**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.

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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
<b>Difference</b>			<b>Base</b>		<b>0.15</b>		<b>0.13</b>		<b>0.15</b>		<b>0.15</b>

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 than 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 6<sup>th</sup> and 7<sup>th</sup> 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<sub>2</sub>, 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 <sub>2</sub>	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 <sub>2</sub> /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 <sup>1</sup>	FEA-1100 <sup>2</sup>	AFA-L1 <sup>3</sup>
Chemical Formula	n/k	n/k	n/k
Molecular Weight	<134	161-165 (est.)	<134
Boiling point (°C)	>15 <32	>33	>15 <30
Gas Conductivity (mWm <sup>-1</sup> K at 10 <sup>0</sup> 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

<sup>1</sup>Honeywell <sup>2</sup>DuPont <sup>3</sup>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 in 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.

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## 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 at 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**).

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### 3. Implementation

The project was approved at the 58<sup>th</sup> 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 6<sup>th</sup> and 7<sup>th</sup> 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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<sup>1</sup> \*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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#### 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 <sup>2</sup> 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:

	<u>Methylal</u>	<u>HCFC-141b</u>
• 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:

**METHYLAL EMISSIONS 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:

- |                                      | <u>Methylal</u> | <u>HCFC-141b</u>  |
|--------------------------------------|-----------------|-------------------|
| • 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 °C
- Peroxide building       - No formation of peroxides has been detected
- Hydrolysis                - Stable under neutral/alkaline conditions (polyols are slightly alkaline)  
                                      - The pH of ML systems matches approximately those of HCFC-141b  
                                      - Very slow (>1 year) hydrolysis under acid condition
- Corrosion                 - No corrosivity determined

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

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

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### 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.

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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 <sup>3</sup>	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 <sup>3</sup>	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 <sup>3</sup>	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 <sup>3</sup>	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
<b>Entire Sample</b>			
Molded Density	Kg/m <sup>3</sup>	348,6	356,7
Hardness	Shore A	52	50
Resilience	%	34	35
<b>Foam Core</b>			
Internal Density	Kg/m <sup>3</sup>	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
<b>Skin Only</b>			
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 types	R-095	R-096	R-099	QZCT15	Test Method
Type		SPORT	TRAVEL	RIGID	SEMI-RIGID	
<b>Blowing Agent</b>	<b>141b</b>	<b>ML</b>	<b>ML</b>	<b>ML</b>	<b>ML</b>	
Density (kg/m <sup>3</sup> )	<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 <sup>3</sup>	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)			
<i>side 1 max</i>	%	6,97	1,67
<i>side 1 min</i>	%	-0,24	-0,81
<i>side 2 max</i>	%	-0,81	-0,90
<i>side 2 min</i>	%	-0,31	0,05
<i>thickness max</i>	%	0,73	4,78
<i>thickness min</i>	%	-0,25	0,13
Dim. Stability (-20 C)			
<i>side 1 max</i>	%	-0,16	0,41
<i>side 1 min</i>	%	-0,01	-0,01
<i>side 2 max</i>	%	-0,59	0,28
<i>side 2 min</i>	%	-0,14	-0,03
<i>thickness max</i>	%	-5,87	-0,92
<i>thickness min</i>	%	-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 <sup>3</sup>	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)			
<i>side 1 max</i>	%	0,85	-0,31
<i>side 1 min</i>	%	-0,11	-0,29
<i>side 2 max</i>	%	-0,35	-0,41
<i>side 2 min</i>	%	0,03	-0,28
<i>thickness max</i>	%	-4,53	-0,57
<i>thickness min</i>	%	-0,18	-0,55
Dim. Stability (-20 C)			
<i>side 1 max</i>	%	0,25	-0,10
<i>side 1 min</i>	%	0,06	-0,06
<i>side 2 max</i>	%	0,10	-0,07
<i>side 2 min</i>	%	0,03	-0,04
<i>thickness max</i>	%	0,21	-0,27
<i>thickness min</i>	%	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 <sup>3</sup>	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)			
<i>side 1 max</i>	%	-1,19	-0,9
<i>side 1 min</i>	%	-0,09	-0,04
<i>side 2 max</i>	%	-0,44	-1,11
<i>side 2 min</i>	%	-0,01	-0,52
<i>thickness max</i>	%	-6,31	-2,85
<i>thickness min</i>	%	-0,91	1,18
Dim. Stability (-20 C)			
<i>side 1 max</i>	%	0,53	-0,08
<i>side 1 min</i>	%	-0,11	-0,02
<i>side 2 max</i>	%	-0,32	-0,32
<i>side 2 min</i>	%	0,05	-0,06
<i>thickness max</i>	%	6,21	-6,26
<i>thickness min</i>	%	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 <sup>3</sup>	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)			
<i>side 1 max</i>	%	-0,58	-0.64
<i>side 1 min</i>	%	-0,16	-0.18
<i>side 2 max</i>	%	-0,56	-0.67
<i>side 2 min</i>	%	-0,19	-0.22
<i>thickness max</i>	%	-4,11	-2.24
<i>thickness min</i>	%	2,32	1.82

Dim. Stability (-20 C)			
<i>side 1 max</i>	%	0,03	0.04
<i>side 1 min</i>	%	-0,01	-0.02
<i>side 2 max</i>	%	0,03	0.04
<i>side 2 min</i>	%	0,01	-.03
<i>thickness max</i>	%	0,09	0.12
<i>thickness min</i>	%	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 <sup>3</sup>	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)			
<i>side 1 max</i>	%	0,43	1,08
<i>side 1 min</i>	%	0,09	0,01
<i>side 2 max</i>	%	0,70	1,94
<i>side 2 min</i>	%	-0,02	0,06
<i>thickness max</i>	%	-1,25	-2,35
<i>thickness min</i>	%	-0,70	-0,63
Dim. Stability (-20 C)			
<i>side 1 max</i>	%	0,20	-0,15
<i>side 1 min</i>	%	0,02	-0,02
<i>side 2 max</i>	%	0,16	0,13
<i>side 2 min</i>	%	-0,02	-0,02
<i>thickness max</i>	%	-6,88	-1,33
<i>thickness min</i>	%	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 <sup>3</sup>	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)			
<i>side 1 max</i>	%	-0,89	0,43
<i>side 1 min</i>	%	-0,08	0,02
<i>side 2 max</i>	%	-1,47	1,65
<i>side 2 min</i>	%	-0,84	0,36
<i>thickness max</i>	%	-3,00	-3,55
<i>thickness min</i>	%	-0,59	0,25
Dim. Stability (-20 C)			
<i>side 1 max</i>	%	-0,05	0,15
<i>side 1 min</i>	%	0,03	-0,01
<i>side 2 max</i>	%	0,04	0,10
<i>side 2 min</i>	%	0,02	0,02
<i>thickness max</i>	%	-0,38	7,39
<i>thickness min</i>	%	-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/m <sup>3</sup>	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)			
<i>side 1 max</i>	%	-0,56	-0,62
<i>side 1 min</i>	%	-0,15	-0,17
<i>side 2 max</i>	%	-0,54	-0,65
<i>side 2 min</i>	%	-0,18	-0,21
<i>thickness max</i>	%	-3,98	-2,17
<i>thickness min</i>	%	2,25	1,76
Dim. Stability (-20 C)			
<i>side 1 max</i>	%	0,04	0,05
<i>side 1 min</i>	%	-0,01	-0,03
<i>side 2 max</i>	%	0,04	0,05
<i>side 2 min</i>	%	0,01	0,04
<i>thickness max</i>	%	0,12	0,16
<i>thickness min</i>	%	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	
System House			
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
<b>Difference</b>			<b>Base</b>		<b>0.15</b>		<b>0.15</b>		<b>0.15</b>		<b>0.15</b>



## 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**

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## 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 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. ML-based systems with less than 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)**

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

## 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.



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

## 1. PROJECT BACKGROUND

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<sup>th</sup> 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 <sup>th</sup> ExCom	Evaluation of cost saving options
Methyl formate	Approved at the 56 <sup>th</sup> ExCom	Technical validation of a commercial available product
Methylal	To be submitted to 58 <sup>th</sup> ExCom	Technical validation of a commercial available product
Supercritical CO <sub>2</sub>	Under development	Technical validation of a commercial available product
HFO-1234ze*	To be submitted to 57 <sup>th</sup> ExCom	Technical validation of a commercial available product

\* A Hydro-Fluoro-Olefin. Full name: trans-1,3,3,3-tetra fluoro propene; CHF=CHCF<sub>3</sub>

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](mailto: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):

<u>Substance</u>	<u>2007</u>	<u>2008</u>	<u>Remarks</u>
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<sub>2</sub> (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:

	<u>Methylal</u>	<u>HCFC-141b</u>
• 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:

	<u>Methylal</u>	<u>HCFC-141b</u>
• 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 <sup>2</sup> 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
<b>Methylal</b>	<b>99.5 % min.</b>	<b>99.9 % min.</b>	<b>99.5 % min.</b>	<b>93 % min.</b>
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

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

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

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

**8. IMPLEMENTATION/MONITORING**

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

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

Phase-II -Prepare individual Implementation plans -Procurement -Installation/start-up -Trials -Certificates of Technical Completion (COCs) -Handover Protocols (HOPs) -Completion Report (PCR)				X	X	XX XX XX X	X	X
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**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
(l) Compliance Monitoring	17

\* As measured from project approval

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

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



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)
<u>Methylal</u>	: > 93 %	000109-87-5 / 203-714-2 / ----	F	11
<u>Methanol</u>	: <= 6.5 %	00067-55-1 / 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.

<b>MATERIAL SAFETY DATA SHEET</b>	Page : 2
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**5. Fire -fighting measures**

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

**6. Accidental release measures**

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

**7. Handling and storage**

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

**8. Exposure controls / personal protection**

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

**9. Physical and chemical properties**

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



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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.
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**14. Transport information**

Hazard Label(s)



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

**15. Regulatory information**

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

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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:  $\text{CH}_3\text{OCH}_2\text{OCH}_3$
- 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 ( $\text{mg}/\text{m}^3$ ).

## 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, light-headedness, 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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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

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

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data

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

### • Reactivity

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

4. Special precautions: Methylal will attack some forms of plastics, rubber, and coatings.

### • Flammability

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

### • Warning properties

1. Odor Threshold: No quantitative information is available concerning the odor threshold, but Browning notes that it has a slightly pungent odor.

2. Eye Irritation Level: Grant states that "exposures of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially were found to cause . . . occasional irritation of the eyes but no histologically demonstrable abnormality of the optic nerve or retina."

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

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

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

## MONITORING AND MEASUREMENT PROCEDURES

### • General

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

### • Method

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

## RESPIRATORS

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

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylal.

• Clothing wet with liquid methylal should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylal from the clothing. If the clothing is to be laundered or

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

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

## SANITATION

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

## COMMON OPERATIONS AND CONTROLS

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

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

## EMERGENCY FIRST AID PROCEDURES

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

### • Eye Exposure

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

### • Skin Exposure

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

### • Breathing

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

### • Swallowing

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

### • Rescue

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

## SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If methylal is spilled or leaked, the following steps should be taken:

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



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

**REFERENCES**

- American Conference of Governmental Industrial Hygienists: "Methylal," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.
- Celanese Corporation: *Product Bulletin - Methylal*, New York.

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

**RESPIRATORY PROTECTION FOR METHYLAL**

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

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



**ATTACHMENT III:**  
**PROCESS EMISSIONS**

**ATTACHMENT IV**  
**TOXICOLOGICAL PROFILE**



Lambiotte & Cie S.A.

**METHYLAL**  
**(DIMETHOXYMETHANE)**  
**TOXICOLOGICAL PROFILE**

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

October 19<sup>th</sup>, 1998

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**ACUTE TOXICITY STUDIES**

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

\* Unless otherwise stated  
NA : Information not available

**ACUTE TOXICITY STUDIES (continued)**

Ref #	Species/strain	Initial Group	Route of administration	Dose mg/kg bw*	Dilution	Document ID	LD 50 mg/kg bw *	Comments	Date	Laboratory
6	Rabbit New Zealand	Total : 10 5 M + 5 F	Topical covered for 24 h	5,000	Undiluted	5	> 5,000	No mortality No treatment related clinical signs nor gross pathology changes	Nov. 1989	Springborn Laboratories, Ohio USA
7	Rabbit New Zealand	Total : 20 10 M + 10 F	Topical covered for 24 h	- 1 ml/kg bw (4 M + 4 F) - 4 ml/kg bw (2 M + 2 F) -16ml/kg bw (4 M + 4 F)	Undiluted	3	> 16 ml/kg bw = 13,760 mg/kg bw	No mortality. Clinical signs at 4 and 16 ml/kg bw Local irritation at 16ml/kg bw Gross pathology changes at 1 and 16 ml/kg bw	Dec. 1982	Bushy Run Research Center, PA USA
8	Mouse ICR	Total : 30 3 M + 3 F per dose	Intraperitoneal	500 1,625 2,750 3,875 5,000	Diluted with 0.9% aqueous sodium chloride	6	> 3,875 < 5,000	Mortality 5 out of 6 mice at 5,000 mg/kg bw Clinical signs at 2,750 and above	June 1990	Hazleton Laboratories, MD USA
9	Guinea Pig NA	NA	Subcutaneous	3.0 ml/kg bw 3.5 5.0	NA	7	> 5 ml/kg bw = 4,300 mg/kg bw	No mortality up to 5 ml/kg bw Local reaction at injection sites	1951	NIH USA
10	Mouse Swiss	(?) groups of 10 animals	Inhalation	NA 7 h exposure		7	LC 50 = 18,354 ppm	Nervous signs preceding 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	LD50 mg/kg bw *	Comments	Date	Laboratory
11	Rat NA	NA	Inhalation	NA		8	LC50= 15,000 ppm	NA	NA	NA
12	Rat Wistar	Total : 30 5 M + 5 F per dose	Inhalation	Saturated vapor 23° C Exposure for 14, 27 or 51 min (males) or 18, 35 or 64 min (females)		3	NA	Death occurred between 14 to 27 min (males) or 18 to 35 min (females) Nervous signs observed	Dec. 1982	Bushy Run Research Center, PA USA
13	Guinea Pig NA	NA	Inhalation	NA		7	NA	Clinical signs and deaths at concentrations around 150,000 ppm in one and a half to two and a half hours.	1951	NIH USA

\* Unless otherwise stated  
NA : Information not available



**LOCAL TOLERANCE STUDIES**

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

NA : Information not available

**MULTIDOSE TOXICITY STUDIES**

Ref #	Test/type	Species/ strain	Initial group	Route of administration	Dose	Docu- ment 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 Administration	Dose PPM	Treatment duration	Document 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 parameters or the macroscopic foetal structure	At 10,000 ppm some clinical signs	1997	Huntingdon Life Science <b>UK</b>
23	Effects on embryo/foetal development by inhalation in the rat	Rat Charles River	Total 100, 1 control and 3 treated groups of 25 mated females each	Inhalation 6 hour daily exposure	0 (control) 400 2000 10,000	From day 6 to 15 of pregnancy	13	At 386 and 1954 ppm: no treatment-related findings. At 10,068 ppm: reduction in body weight gain between Days 6 and 12 of pregnancy and food intake between Days 6 and 16 of pregnancy. Water intake markedly higher than controls during Days 8 to 19 post coitum.	No changes considered to be related to exposure to methylal. Exposure of the parent female to 10,068 ppm has no effect on embryo-foetal development.	No effect exposure level: 1954 ppm.	1997	Huntingdon Life Science <b>UK</b>

**MUTAGENICITY STUDIES**

Ref #	Study type	Study description	Treatment	Docu- ment ID	Result	Date	Laboratory
24	Ames test	In vitro genotoxicity in <i>S. Typhimurium</i> 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 <i>S. Typhimurium</i> strains (TA 1535 - TA 1537 - TA 98 and TA 100) and <i>E. Coli</i> 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 CHOHPRT forward mutation assay	Exposure of CHO cells to the test substance and selection of mutants at the HGPRT locus as able to form colonies in the presence of 6-thio-guanine	0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/ml with and without metabolic activation	16	Toxicity at concentrations above 1000 µg/ml No mutagenic activity both in presence or in absence of metabolic activation	Oct. 1990	Hazleton Laboratories, MD USA
27	Mouse micronucleus test	Evaluation of the micronuclei in bone marrow polychromatic erythrocytes of mice. 5 M and 5 F ICR mice per dose/harvest time group. Harvest time at 24 h, 48 and 72 h	Single intraperitoneal injection at doses of 400, 1333 and 4000 mg/kg bw	17	No significant increase in micronuclei in bone marrow polychromatic erythrocytes	July 1990	Hazleton Laboratories, MD USA

**SPECIAL TOXICITY STUDIES**

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





## **DOCUMENTS**

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

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

Gig. Truda, 1984, n° 6, 27-29

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

Biochemical Research Laboratory, The Dow Chemical Company

December 16<sup>th</sup>, 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 7<sup>th</sup>, 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 22<sup>nd</sup>, 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 14<sup>th</sup>, 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 3<sup>rd</sup>, 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 27<sup>th</sup>, 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 20<sup>th</sup>, 1989.

EPA/OTS Doc # 86-900000004

EPA/OTS 0521278

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

Huntingdon Life Sciences Ltd, Huntingdon, England.

July 23<sup>rd</sup>, 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 10<sup>th</sup>, 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 25<sup>th</sup>, 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 11<sup>th</sup>, 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<sup>2</sup>:

- **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"<sup>3</sup>. 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:

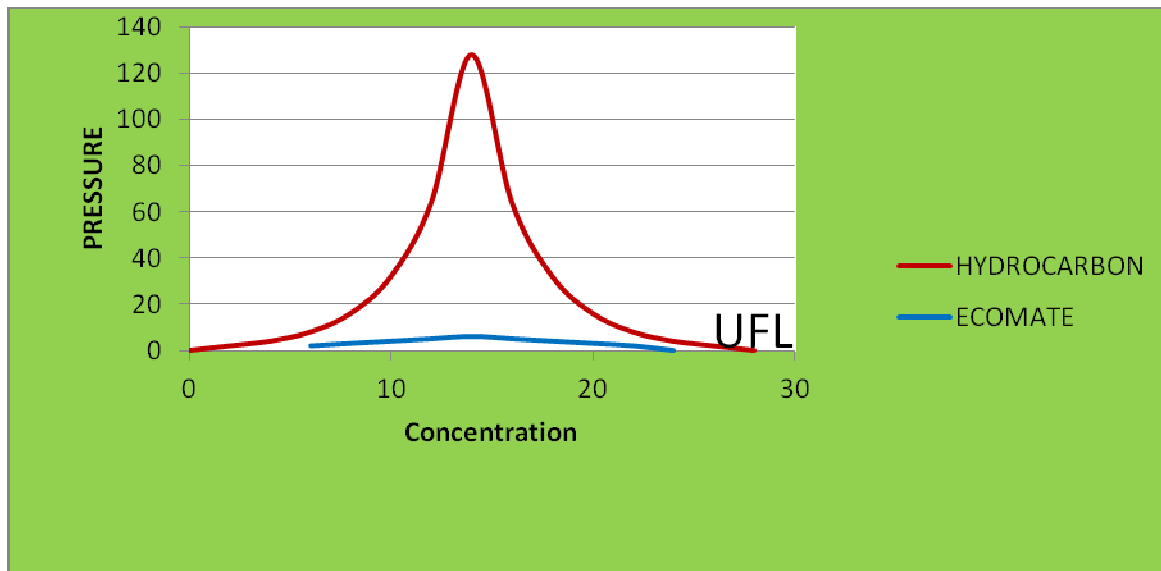
Substance	Heat of Combustion (kcal/g)	Comments
HCFC-141b	1.9	
Methyl Formate	3.9	
Methylal	6.1	
Ethanol	7.1	
Pentane (commercial mix)	11.5	Cyclopentane estimated ~10% lower

<sup>2</sup> Panov, G.E. and Polozkov, V. T.. "Flammable Substances", Encyclopedia of Occupational Health and Safety, 3<sup>rd</sup> Edition, International Labor Office Geneva, pp. 881-883 (1983)

<sup>3</sup> 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  $-18^{\circ}\text{C}$  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  $120^{\circ}\text{F}$  (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 °C; substance emissions under legal exposure limits) as the following calculations show:

#### Methylal

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

#### HCFC-141b

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

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

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

#### 4. CONCLUSIONS/RECOMMENDATIONS

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

In view of the foregoing, following recommendations are offered:

1. System houses, who process pure grade methylal should have
  - Proper personal protective equipment;
  - Closed blending containers, with a dry nitrogen blanket;
  - Explosion proof equipment (pump, agitator, light, heating/cooling,);
  - Electrically grounded equipment and drums (grounding clip);
  - A methylal vapor sensor with alarm function set on 20% LFL;
  - Adequate ventilation;
  - Meter Methylal under the level of the liquid to which it is being added.
2. Downstream users, who process polyol and/or Isocyanate blends should have
  - Proper personal protective equipment;
  - Electrically grounded equipment and drums (grounding clip);
  - A methylal vapor sensor with alarm function set on 20% LFL;
  - Adequate ventilation.

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

5.

**ATTACHMENT VI**  
**ECOTOXICOLOGICAL PROFILE**

Lambiotte & Cie S.A.

**METHYLAL**  
**(DIMETHOXYMETHANE)**  
**ECOTOXICOLOGICAL PROFILE**

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

April 21<sup>st</sup>, 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<sub>50</sub> > 1000 mg/l

48 h EC<sub>50</sub> > 1000 mg/l

NOEC = 1200 mg/l

The 48-h LC<sub>50</sub> and the 48-h EC<sub>50</sub> 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<sup>-1</sup>.

### Fish

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

96 h LC<sub>50</sub> > 1000 mg/l

96 h EC<sub>50</sub> > 1000 mg/l

NOEC = 1000 mg/l

The 96-h LC<sub>50</sub> and the 96-h EC<sub>50</sub> 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<sup>-1</sup> (NOEC).

This value is based on the nominal concentration of methylal. NOEC = 700-800 mg.l<sup>-1</sup> (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
<b>Polyol</b>	83,16	100,00	82,08	100,00
<b>Cross-linker</b>	0,92	1,11	0,90	1,10
<b>Silicone</b>	0,27	0,32	0,11	0,13
<b>Additive</b>	2,08	2,50	0,00	0,00
<b>Catalyst A</b>	0,83	1,00	0,52	0,63
<b>Catalyst B</b>	1,00	1,20	0,56	0,68
<b>Water</b>	1,24	1,49	1,22	1,48
<b>Methylal</b>	10,50	12,63	0,00	0,00
<b>HCFC-141b</b>	0,00	0,00	14,61	17,80
<b>Total</b>	100,00	120,25	100,00	121,82

STRUCTURAL FOAM

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

NON-CONTINUOUS BLOCK

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

SPRAY

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

TRANSPORTATION

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

THERMOWARE

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

WATER HEATER

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

HIGH RESILIENCE MOLDED

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

VISCOELASTIC

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

VISCOELASTIC BLOCKS (NON CONTINUOUS)

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



STEERING WHEELS

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

FURNITURE

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

**ATTACHMENT VIII**  
**PARTICIPATION LETTERS OF DOWNSTREAM USERS**

# MATERIAL SAFETY DATA SHEET

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Revision nr : 5

Date : 30/9/2005

Supersedes : 20/2/2004

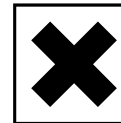
## METHYLAL TECHNICAL GRADE

**L-9307**

www.lisam.com



Highly flammable



Harmful

### Producer

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

### 1. Identification of the product and the company

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

### 2. Information on ingredients

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

Substance name	Value(s)	CAS nr / EINECS nr / EC index	Symbol(s)	R-Phrase(s)
<u>Methylal</u>	: > 93 %	000109-87-5 / 203-714-2 / ----	F	11
<u>Methanol</u>	: <= 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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### 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.
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### 14. Transport information

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

### 15. Regulatory information

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

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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:  $\text{CH}_2\text{OCH}_2\text{OCH}_2$
- 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 ( $\text{mg}/\text{m}^3$ ).

## 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, light-headedness, 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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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

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.

• 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.

## 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.

## RESPIRATORY PROTECTION FOR METHYLAL

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

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



## 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/m<sup>3</sup> = miligrama por metro cúbico; mg = miligrama; µg = micrograma; NI = não informado; "<" = abaixo do LQ; f/cc = Fibra por centímetro cúbico; NE = não estabelecido.

São Bernardo do Campo, 31/10/2011

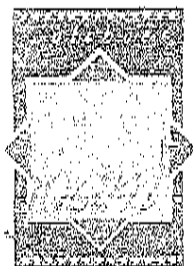
Oscar Shigueo Umemura

CRQ IV 04218265

Supervisor do Laboratório

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

Suzano 19 de agosto de 2011



## DECLARAÇÃO

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

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

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, Rígido 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 expensor 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 Ltda.

Farroupilha - RS, 03 de março, 2011.

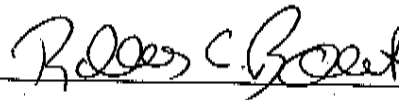
## DECLARAÇÃO

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 expensor HCFC 141b.

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

Atenciosamente,



Nome: Robson Colombo Balbinot

Cargo: Analista de Crescimento

Empresa: Soprano

Local, data, ano  
Cambe' PR

02/06/2011

## 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 expensor 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  
do Rian - CEP 86187-000

CAMBE - PR

Nome: Claudio Roberto Balsanelo

Cargo: Encarregado Produção

Empresa: Furgão Roma



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 expensor HCFC 141b.

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

Atenciosamente,



Nome: Sérgio José Correa

Cargo: Diretor Comercial





**PURAPELE**

## **MANUFATURA DE PELES FLORENSE LTDA.**

VILA NOVA ROMA - 95270-000 - FLORES DA CUNHA - RS

FONE / FAX: (054) 292-2130

INSC. CGCMF Nº 89.968.390/0001-00 - INSC. ESTADUAL Nº 048/0002630

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

### **DECLARAÇÃO**

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

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como, aspecto do sistema incorporado com o agente expensor 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@mfczinhas.com.br](mailto:cookmachine@mfczinhas.com.br)  
Home Page: [www.mfcozinhas.com.br](http://www.mfcozinhas.com.br)

*São Caetano do Sul, 14 de Abril de 2011*

### **DECLARAÇÃO**


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

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

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

*Atenciosamente*

MF COZINHAS INDUSTRIAIS LTDA.

  
Sílvia Maria Ap. Saltini Filleti  
Diretora

São Paulo, 07 de Abril de 2011.

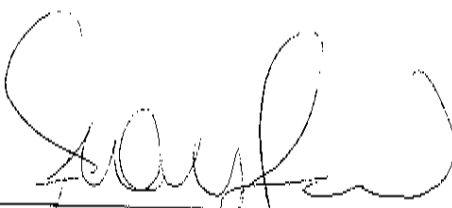
## DECLARAÇÃO

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 expensor 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

Santana de Parnaíba, 07 de abril de 2011.

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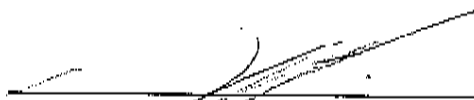
## DECLARAÇÃO

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 expensor HCFC 141b.

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

Atenciosamente,



---

**POLIURETANOS BRASIL LTDA**  
Rafael Santamaria Sarmiento



v i t t a f l e x

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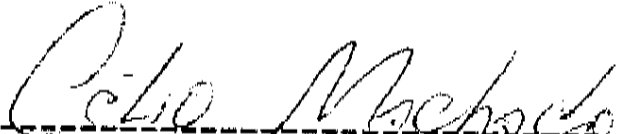
espumas especiais

### *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 expensor HCFC 141b. Portanto, o sistema com *methylal* atende todas as nossas necessidades técnicas e produtivas.

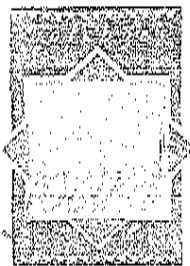
Atenciosamente



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**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 expensor 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**

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**AN ASSESSMENT FOR APPLICATION IN MLF  
PROJECTS**

**MARCH 2012**

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## EXECUTIVE SUMMARY

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

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

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

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

UNDP saw options for cost reduction in the following areas:

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

The project was executed in three steps:

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

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

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

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

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

For the systems development six different systems were selected:

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

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

All systems were tested on

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

The tests showed that

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

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

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

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

The outcome of these follow-up investigations will be published in a supplemental report, expected to be presented to the 67<sup>th</sup> 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<sup>0</sup>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<sub>2</sub>), 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 <sup>1</sup>	MOLECULAR WEIGHT	INCREMENTAL GWP <sup>2</sup>	COMMENTS
HCFC-141b	725	117	Baseline	
CO <sub>2</sub>	1	44	-725	Used direct/indirect (from water)
Cyclopentane	11 <sup>2</sup>	72	-718	Extremely flammable
<b>HFC-245fa</b>	<b>1,030</b>	<b>134</b>	<b>443</b>	
<b>HFC-365mfc</b>	<b>794</b>	<b>148</b>	<b>279</b>	
<b>HFC-134a</b>	<b>1,430</b>	<b>102</b>	<b>522</b>	
Methyl formate	negligible	60	-725	
Methylal	negligible	76	-725	
Acetone	negligible	58	-725	Used in flexible slabstock
FEA-1100	5	164 <sup>4</sup>	-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

<sup>1</sup> Unless otherwise indicated, taken from IPCC’s Fourth Assessment (2007)

<sup>2</sup> 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

<sup>3</sup> From UNEP Foams Technical Options Committee’s 2006 report

<sup>4</sup> 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<sup>th</sup> 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<sup>1</sup>
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 **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

The bidding process led to the selection of SAIP/Pozzi-Arioso for both system and equipment development. SAIP/Pozzi suggested—and UNDP accepted—to team up for its system development with Dow Systems, Italy and for trials with Dow Systems, Egypt. This arrangement has worked out very well as will be shown in this report and UNDP wants to express its appreciation to the project collaborators.

For more details on design, related budget, etc., it is referred to the project document in its approved version (**ATTACHMENT-III**).

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<sup>1</sup> (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 <sub>2</sub> H <sub>3</sub> Cl <sub>2</sub> F	C <sub>5</sub> H <sub>12</sub>	C <sub>5</sub> H <sub>12</sub>	C <sub>5</sub> H <sub>10</sub>
Molecular Weight	117	72	72	70
Boiling point (°C)	32	36	28	50
Gas Conductivity (mWm <sup>0</sup> K at 25 °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 <sup>0</sup> 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)
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 °C would be ~ 11;

\*\* Extrapolation at 25 °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:

	<u>Cyclopentane</u>	<u>HCFC-141b</u>
• 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:

	<u>Cyclopentane</u>	<u>HCFC-141b</u>
• 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°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/OzI.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 10<sup>th</sup> 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.

- o **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.
- o **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.;**
- o **Safeguard areas that cannot be reclassified, through explosion proofing;**
- o **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;**
- o **Provide adequate emergency response gear such as firefighting equipment;**
- o **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;**
- o **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**

- o Location and installation of storage systems for hydrocarbons are subject to local regulations..
- o 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.
- o 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.
- o Nitrogen blanketing shall be provided.
- o All components shall be properly grounded.
- o Protection against lightning may be required depending on location.
- o All installations within 4 m radius of the tank shall meet Zone 1 requirements.
- o Minimal one gas detector, connected to the central gas sensing and alarm system, shall be installed.
- o At a minimum two portable fire Extinguishers shall be installed.
- o 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.
- o The CP transfer pump, if included, shall be explosion proof with backflow protection.

## **PREBLENDER**

- o The preblender shall be placed in/on a spill containment of sufficient size.
- o It shall be placed in an enclosure, connected to an adequately sized two stage air extraction system that allows 6/10 air replacements/hour.
- o One gas detector shall be installed, attached to the central gas sensing and alarm system.
- o 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.
- o All equipment inside the enclosure shall meet Zone 1 requirements.
- o All equipment shall be properly grounded.

## **FOAM DISPENSER**

- o Tanks shall be placed in/on individual spill containment of sufficient size.
- o 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.
- o Drip pans shall be placed under metering pumps.
- o All installations in the enclosure shall meet Zone 1 requirements.
- o At a minimum one gas detector shall be installed, attached to a central gas sensing and alarm system.
- o Minimal two 6 kg ABC portable fire extinguishers shall be installed close to the foam dispenser.
- o All equipment shall be properly grounded.

## **MOLDS, FIXTURES, PRESSES**

- o 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.
- o 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.
- o 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**

	<b>REQUIREMENTS</b>	<b>OK</b>	<b>COMMENTS /ACTIONS</b>
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<sup>0</sup>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<sub>2</sub>), 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 <sup>1</sup>	MOLECULAR WEIGHT	INCREMENTAL GWP <sup>2</sup>	COMMENTS
HCFC-141b	725	117	Baseline	
CO <sub>2</sub>	1	44	-725	Used direct/indirect (from water)
Cyclopentane	11 <sup>2</sup>	72	-718	Extremely flammable
<b>HFC-245fa</b>	<b>1,030</b>	<b>134</b>	<b>443</b>	
<b>HFC-365mfc</b>	<b>794</b>	<b>148</b>	<b>279</b>	
<b>HFC-134a</b>	<b>1,430</b>	<b>102</b>	<b>522</b>	
Methyl formate	negligible	60	-725	
Methylal	negligible	76	-725	
Acetone	negligible	58	-725	Used in flexible slabstock
FEA-1100	5	164 <sup>4</sup>	-718	Under development

HFO-1234ze	6	114	-719	Recently introduced
HBA-2	<15	<134	>-708	Under development
AFA-L1	<15	<134	>-708	Under development

<sup>1</sup> Unless otherwise indicated, taken from IPCC's Fourth Assessment (2007)

<sup>2</sup> Derived from comparing GWP's 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

<sup>3</sup> From UNEP Foams Technical Options Committee's 2006 report

<sup>4</sup> 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 its 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 <sub>5</sub> H <sub>12</sub>	C <sub>5</sub> H <sub>12</sub>	C <sub>5</sub> H <sub>10</sub>
Molecular Weight	72	72	70
Boiling point (°C)	36	28	50
Gas Conductivity (mWm <sup>0</sup> K at 25 °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 <sub>2</sub> FCF <sub>3</sub>	CF <sub>3</sub> CH <sub>2</sub> CHF <sub>2</sub>	CF <sub>3</sub> CH <sub>2</sub> CF <sub>2</sub> CH <sub>3</sub>
Molecular Weight	102	134	148
Boiling point (°C)	-26.2	15.3	40.2
Gas Conductivity (mWm <sup>0</sup> K at 25 °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 <sub>2</sub>
Molecular Weight	44
Boiling point (°C)	-78
Gas Conductivity (mWm <sup>0</sup> K at 25 °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<sub>2</sub> 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 a 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<sub>2</sub> 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<sup>®</sup>)

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<sup>®</sup>, 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 °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	Not available	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, 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 <sub>3</sub>	n/k	n/k	n/k
Molecular Weight	114	<134	161-165 (estimated)	<134
Boiling point (°C)	-19	>15 <32	>25	>10 <30
Gas Conductivity (mWm <sup>0</sup> K at 10 °C)	13	n/k	10.7	10
Flammable limits in Air (vol. %)	None	None	None	None
TLV or OEL (ppm; USA)	1,000 (proposed)	n/k	n/k	n/k
GWP (100 y)	6	<15	5	Negligible
ODP	0	0	0	0

Since early 2008, several new blowing agents for PU foams have been proposed by major international manufacturers of halogenated compounds. Four of them are worth mentioning. These are all geared towards replacement of HFCs and sometimes called "second generation" HFCs, although HFOs appear to have a more distinctive description. They share low/no flammability, zero ODP and insignificant GWPs:

Except HFO-1234ze, all other chemicals listed out in the table above will not be commercialized in the next few years and, most likely, will then first be geared towards developed countries where legal limitations on HFCs are considered. It may appear somewhat late in an A5 context where foam conversion is prioritized. As to HFO-1234ze, this is already in use as a replacement of HFC-134a in one component foams (OCF). There are only few OCF manufacturers in developing countries.

**ATTACHEMENT III:**

**Project on Validation/Demonstration of Low Cost Options for the Use of Hydrocarbons as foaming agent in the Manufacture of PU Foams**

<b>COUNTRY:</b>	Egypt
<b>IMPLEMENTING AGENCY:</b>	UNDP
<b>PROJECT TITLE:</b>	Validation/Demonstration of Low Cost Options for the Use of Hydrocarbons as foaming agent in the Manufacture of PU Foams
<b>PROJECT IN CURRENT BUSINESS PLAN:</b>	Based on ExCom Decision 55/43(e i-iii)
<b>SECTOR:</b>	Foams
Sub-Sector:	Rigid and Integral Skin PU Foams
<b>ODS USE IN SECTOR</b>	
Baseline:	Not yet determined
Current (2007):	433 ODP t HCFCs as per Government reporting
<b>BASELINE ODS USE:</b>	n/a (pilot project)
<b>PROJECT IMPACT (ODP targeted):</b>	n/a (pilot project)
<b>PROJECT DURATION:</b>	8 months
<b>PROJECT COSTS:</b>	US\$ 473,000
<b>LOCAL OWNERSHIP:</b>	100 %
<b>EXPORT COMPONENT:</b>	0 %
<b>REQUESTED MLF GRANT:</b>	US\$ 473,000
<b>IMPLEMENTING AGENCY SUPPORT COST:</b>	US\$ 35,475 (7.5 %)
<b>TOTAL COST OF PROJECT TO MLF:</b>	US\$ 508,475
<b>COST-EFFECTIVENESS:</b>	11.8 US\$/kg-ODS
<b>PROJECT MONITORING MILESTONES:</b>	Included
<b>NTL. COORDINATING AGENCY:</b>	Egypt Environmental Affairs Agency (EAAA) 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 58 <sup>th</sup> 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 58 <sup>th</sup> ExCom	Technical validation of a commercial available product
HFO-1234ze	XPS	to 58 <sup>th</sup> 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 or 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.

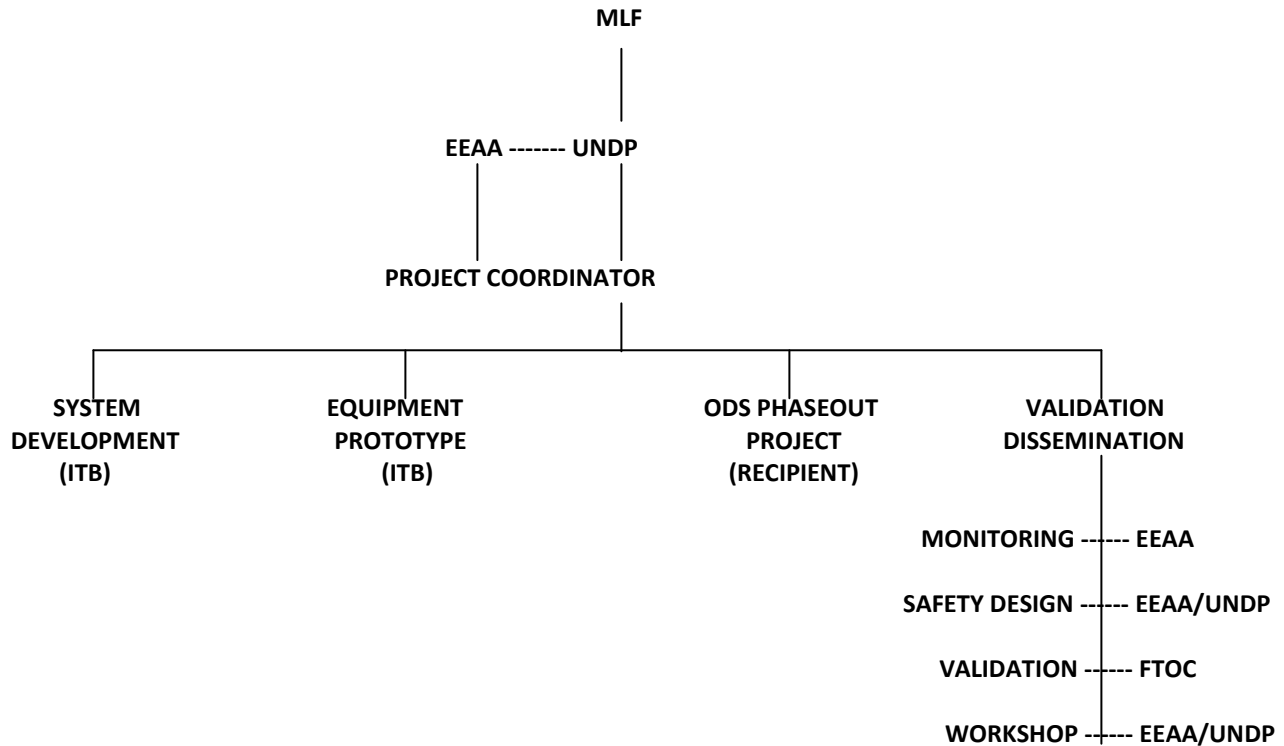
As hydrocarbons are “highly flammable”, UNDP considers the process at the system house (blending) AND at user level (processing) hazardous and requiring adequate safeguards. Current safety requirements are described in UNEP/OzL.Pro/ExCom/25/54 (**Annex 2**). UNDP requires an independent safety audit 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<sub>2</sub> (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<sub>2</sub> as cell gas;
- Technologies such as HBA-2, AFA-L1 and FEA 1100 are not ready for commercialization.

PU validation may therefore be limited to optimized hydrocarbons, methyl formate and methylal.

#### 4.2 HYDROCARBONS AS REPLACEMENT TECHNOLOGY FOR HCFC-141b

HC-based/MLF-supported CFC-phaseout projects have been, along with HCFC-141b, the technology of choice in most refrigeration and in panel applications. The minimum economic size has been typically around 50 ODP t/y or ~US\$ 400,000. For domestic refrigeration a handicap was allowed for safety cost, increasing the threshold to ~US\$ 600,000. Smaller projects could not pass cost-effectiveness criteria. Consequently, there is no use of HCs in SMEs. In addition, the technology was deemed unsafe for a multiple of applications such as spray and in situ foams. There have been attempts to introduce the use of HCs in those applications—even specially modified equipment was developed for that purpose—but the market has not accepted the use of HCs under what it considers “uncontrolled” conditions. Initially, cyclopentane in different degrees of purity has been used for refrigeration, n-pentane for panels and, not very important in an A5 context, more volatile HCs in one-component foams (OCFs). Fine tuning through HC blends (cyclo/iso pentane or cyclopentane/isobutane) which is now standard in non-A5 countries has not widely spread in A5’s. Investment costs are largely the same as at the time of phasing out CFCs. Consequently, the technology would continue to be too expensive for SMEs and restricted to the same applications as before. However, there are options to fine-tune project costs and investigate other applications:

- The introduction of HC blends that will allow lower densities (lower IOCs)
- Direct injection (lower investment)
- Low-pressure/direct injection (lower investment)
- Centralized preblending by system houses (lower investment)
- Application-specific dispensing equipment (lower investment)

Lowering the conversion costs—either by lowering investment or lowering operating costs—will lower the current eligibility barrier of ~50t/y ODS (based on the current applicable threshold) and widen the pool of potentially eligible users. Important in all these considerations, is that for HC, current incremental operating costs are among the lowest of all replacement technologies. Therefore, from an economic standpoint the use of HCs is one of the most important technologies.

#### 5. PROJECT COSTS

Cost forecasts for pilot projects are problematic as these projects are by nature unpredictable. UNDP has used to the extent possible guidance provided by the Secretariat in Doc 55/47 Annex III, Appendix II. Applying this guidance leads to the following summarized cost expectations:

DEVELOPMENT/OPTIMIZATION/VALIDATION/DISSEMINATION			
#	ACTIVITY	BUDGET (US\$)	REMARKS
1	Project Management	10,000	Local expert; see also remark 1
2	Technology transfer, training	30,000	International Expert(s)
3	Testing equipment	55,000	See remark 2 hereunder
4	Production equipment development	125,000	Three-stream high pressure pentane dispenser with standardized, built-in and auxiliary, safety features (modular concept preferred)
5	Preblended systems preparation	100,000	Development: 40,000

			Optimization: 40,000 Validation: 20,000 (at the recipient)
6	Technology Dissemination Workshop	60,000	See remark 3 here-under
7	Peer review/Safety review/Preparation	50,000	Includes - safety audit - design study for centralized HC blending - review by FTOC
8	Contingencies	43,000	10% of sub-total/rounded
<b>TOTAL</b>		<b>473,000</b>	

**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)
	<u>Cell gas analyzer</u>	<u>20,000</u>
	<b>Total</b>	<b>US\$ 55,000</b>

**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				
-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<sup>1</sup>

### 1. Introduction

Current hydrocarbon (HC) technology is based on in-house preblending of the hydrocarbon with a polyol blend, followed by the actual foam process. UNDP requested SAIP to commission equipment for a pilot project in Egypt that would be able to operate with preblended systems as well as to directly inject pentane into the mixing head (“three component system”) without jeopardizing safety.

This paper addresses the use of

- Currently common HC technology (inhouse preblending);
- Preblended HC systems; and
- Directly injected HCs

It then proceeds with describing the equipment as commissioned and tried in the mentioned pilot project.

### 2. Currently Common Equipment for HC Technology

The objective of this part of the presentation is to provide an overview of the most common technology for the use of hydrocarbons (HCs) as an alternative blowing agent to HCFCs in polyurethane foam processing for insulation applications.

The use of HCs is a today proven technology which can be:

- Cost effective
- Easy, economical to operate and commercially available
- Easy and convenient processing
- Occupational safe
- Environmental safe

Whatever the applications of HC’s are, the versatility of the available solutions provides a high degree of flexibility and efficiency.

In the discontinuous foaming process a two component foam dispensing machine is used. The Polyol is inhouse preblended with the blowing agent.

The HC is blended with Polyol through the use of dedicated equipment. HC’s and the Polyol are supplied from storage devices and then metered, through a controlled, closed loop system, by dedicated pumps to the premixing station, where they are mixed through a static mixer.

After completion of the mixing process, the Polyol / HCs blend is transferred with a transfer pump to the high pressure foam dispensing machine (s) Polyol tank (s) through a distribution piping or automatically loaded into a buffer tank and then transferred to the highpressure foam dispensing machine(s) polyol tank(s) through distribution piping.

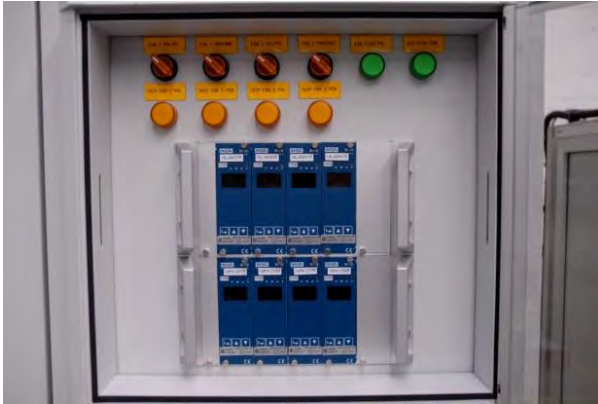
All equipment such as:

- The premixing station
- The buffer tank and the transfer pump
- The foam dispensing machine Polyol

are enclosed in a safety box in order to limit the HCs vapors emissions in a controlled and restricted area. The safety box is provided with safety devices which include double speed fans for forced ventilation complete with suction hoods, extraction chimney, airflow control, detection system (catalytic or infrared sensors) and a safety electric control system (ECS) for management and monitoring of HC vapor emissions.

The safety electric control system (ECS) must be provided with an independent electric power connection in order to guarantee the monitoring and the management of the safeties in case of electric power shut down. The ECS provides the equipment with standard working conditions with one fan in standard operation while starting automatically a second fan with visual and acoustic indication signals if 15% of the LFL (lower explosion level ) is reached. The safety electric control system will shut down the electric power and the HCs feeding at 30% of the LEL.

<sup>1</sup> Presentation to the UNDP workshop on “Innovative Low Cost Hydrocarbon Technologies” in Cairo, Egypt July 4, 2011



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

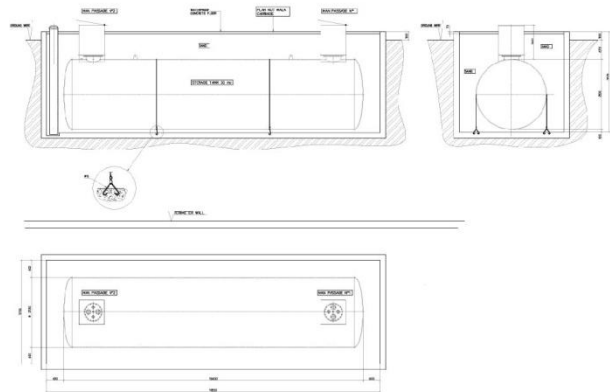
Activities required to introduce HCs in a production facility vary according to geographical area, size of the enterprise, type of production and conditions of the existing facilities.

The use of HCs as blowing agent in polyurethane foam doesn't imply deep changes in the production process but at a minimum the installation of:

- an appropriate HCs storage farm
- a Polyol storage farm (if required )
- the installation of a Polyol / HCs premixing station and related equipment
- the retrofit or the replacement of the foam dispensing machine (s)
- the modifications or the changes, where necessary, of the auxiliaries equipment
- ( foaming fixtures, presses, moulds, etc. )
- the installation of the appropriate safety devices for the monitoring and management of the HCs vapours emissions.

### The HCs storage farm

HCs are stored in double jacket carbon steel tank (s) , that are placed underground in a reinforced concrete basin or above ground.



The tank(s) are equipped with a proper HC's leakage detection system and are placed in a dedicated area outside the production factory. The tank (s) capacity is in relation to the production consumption. The HCs feeding, from the outdoor storage to the indoor premixing station, is provided by volumetric or pneumatic pumps. The HCs feeding piping to the premixing station is placed partially outdoor and partially indoor and can be assembled underground or above ground. The piping can be manufactured in carbon steel and as a single jacket , as a double jacket with HCs leakage control and with or without external insulation. The single jacketed piping is used above ground in outdoor placement and it is normally externally insulated. The double jacketed piping is used either outdoor and underground in order to prevent HCs leakage with consequent ground contamination, or indoor in order to prevent from fire. Moreover particular precaution in the manufacturing of the double jacketed piping must be taken into consideration in case of areas subject to heart quakes. All the piping must be welded while the flanged or threaded connections should be reduced to the minimum and monitored if indoor.



### The 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 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 foam dispensing machine

The foam dispensing machine is a specially designed equipment suitable for the use of HCs, where the Polyol line is enclosed in a safety box which is provided with all the necessary safety devices.

There are different options related to the foam dispensing machine retrofit or replacement as follows:

- replacement with a complete new equipment
- retrofit of the equipment polyol line where applicable
- retrofit of the polyol line with line replacement

Replacement: The complete new equipment would be composed of:

The isocyanate line in a standard configuration

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



## The polyol blend line

- Enclosure and ventilation
- Drip pan
- Pipes, hoses, fittings leakage free
- Tank blanketing with nitrogen
- Grounding
- Detection system ( sensors )
- ATEX components ( e.g. tank levels, tank heating elements, etc. )
- Magnetic coupling for the dosing pump with motor
- Magnetic coupling for the tank stirrer with motor

The polyol line meets European standard ATEX 94/9/EC and is in conformity to II 2 Gc IIB T4.

### The mixing head

High pressure self cleaning linear or laminar flow at two components and provided with nitrogen flushing prior the pouring into a closed cavity. All electric components assembled on the mixing head are ATEX standard.

### The retrofit of the equipment polyol line where applicable

It consist on the replacement of all the components of the line to be in compliance with the ATEX safety standard. This method is applicable to those equipment where conditions are applicable and not high costs are involved.

### The retrofit of the polyol line with line replacement

It consist on the replacement of the whole Polyol line. This method is applicable to those equipment where conditions are not applicable for the retrofit of the components of the Polyol line to be in compliance with the ATEX safety standard.



### The auxiliaries equipment

Very important is the retrofit of the auxiliaries equipment such as foaming fixtures, moulds, foaming presses, etc. to avoid the pentane concentration and the ignition source.

The retrofit consist in the application of:

- A proper ventilation and exhaust system
- A proper detection system ( sensors )
- The grounding of the equipment
- The use of ATEX components

### The zones classification

An important aspect for the conversion of a production facility to the use of HC and the retrofit of the auxiliaries equipment, is the zones classification.

Zones are classified according to the European Directive CEI EN 6007910 in : Zone 0, 1 and 2.

The zone classification is defined in respect of different factors such as pentane vapours emission and their accumulation in the area and the ambient ventilation in the area. That is why, detection and forced artificial and localized ventilation is required as well as other safety measures to avoid ignition sources.



### 3. Preblended HC Systems

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

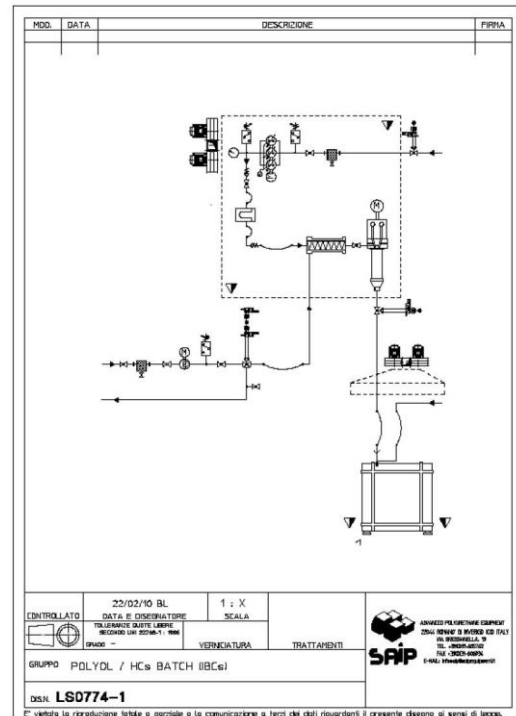


The advantage of using Polyol / HC blends supplied through IBCs is that there is no need to install an HC storage farm and a Polyol / HC premixing station.

The foaming equipment retrofit or replacement concept remains unchanged and as follows :

- replacement with a complete new equipment
- retrofit of the equipment polyol line where applicable
- retrofit of the polyol line with line replacement

Concerning retrofit of auxiliary equipment such as foaming fixtures, moulds, foaming presses, etc., as previously mentioned, the same concept applies to avoid pentane concentrations and the ignition sources. Zoning remains according to the European Directive CEI EN 6007910 in : Zone 0, 1 and 2. The zone classification is defined in respect of different factors such as pentane vapours emission and their shell life in the area and the ambient ventilation in the area. That is why, detection and forced artificial and localized ventilation is required as well as other safety measures to avoid ignition sources.



### 4. Directly injected HCs

HC's can also be injected as third stream directly into the mixing head.

For the third stream injection the following equipment is needed:

- an appropriate HC's storage farm
- a HC's high pressure dosing unit complete with cabin and ventilation
- a high pressure mixing head with third stream
- the modifications or the changes, where necessary, of the auxiliaries equipment ( foaming fixtures, presses, moulds, etc. )
- the installation of the appropriate safety devices for the monitoring and management of the HCs vapours emissions.

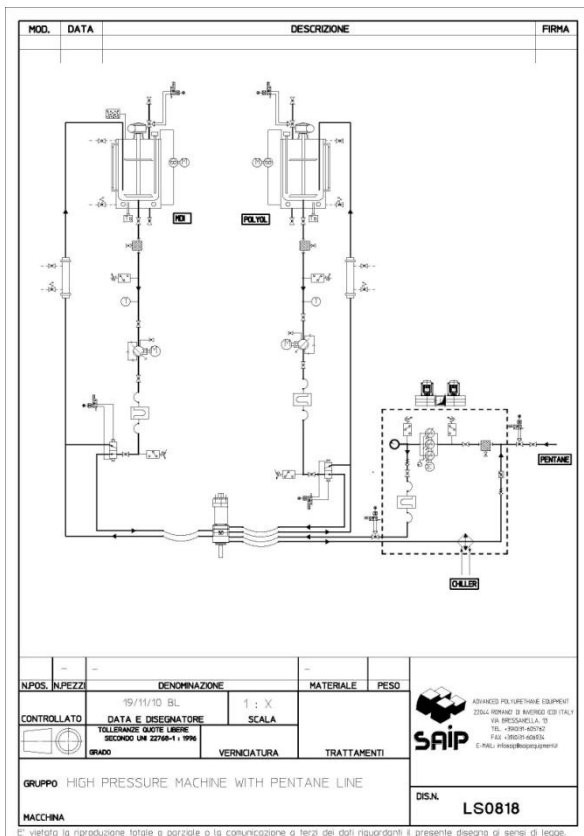
This technology presents a series of advantages:

- With third stream injection the existing 2 component dosing equipment can be used
- There is no need for a premixing station
- No losses of HC's during premixing, shelf life etc.
- No issues with contamination in case different polyols will be used
- Third stream injection allows to change the HC percentage at every shot

Concerning retrofit of auxiliary equipment such as foaming fixtures, moulds, foaming presses, etc., as previously mentioned, the same concept applies to avoid pentane concentrations and the ignition sources. Zoning remains according to the European Directive CEI EN 6007910 in : Zone 0, 1 and 2. The zone classification is defined in respect of different factors such as pentane vapours emission and their shell life in the area and the ambient ventilation in the area. That is why, detection and forced artificial and localized ventilation is required as well as other safety measures to avoid ignition sources.

## 5. The Egypt pilot project – Equipment development

The UNDP project intends to optimize, validate and disseminate the use of low cost hydrocarbon technology in the manufacture of PU rigid insulation for small and medium sizes enterprises. For this purpose UNDP requested foam dispensing equipment that is able to use a premixed Polyol / HC blend along with the option to metering HC as a third stream directly into a mixing and pouring head.



The resulting equipment is a three components dispensing unit and composed as follows :

### The isocyanate line in a standard configuration

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

components

### The polyol / HC blend line

- Enclosure and ventilation
  - Drip pan
  - Pipes, hoses, fittings leakage free
  - Tank blanketing with nitrogen
  - Grounding
  - Detection system (sensors)
  - EX–proof components (tank levels, tank heating elements, etc.)
  - Magnetic coupling for the dosing pump with motor
  - Magnetic coupling for the tank stirrer with motor
  - Closed loop mixing device (static mixer)
- The polyol line meets European standard ATEX 94/9/EC and is in conformity to II 2 Gc IIB T4.

### The HC line

- Enclosure and ventilation
- Drip pan
- Pipes, hoses, fittings leakage free
- Tank blanketing with nitrogen
- Grounding
- Detection system ( sensors )
- EX – proof components
- Magnetic coupling for the dosing pump with motor
- Magnetic coupling for the tank stirrer with motor

The HC line meets European standard ATEX 94/9/EC and is in conformity to II 2 Gc IIB T4.

### The mixing head

High pressure self cleaning laminar flow at three components and provided with nitrogen flushing device. All the electric components assembled on the mixing head are ATEX standard.



### 6. Conclusions

The aim of the project, as mentioned before, is to compare the foam characteristics of 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



## 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)	$\lambda_{\text{gas}}$ at 25°C (mW/mK)	Boiling pt (°C)	Vapor P @ 20°C (bars)	Flammability Limit (% vol. in air)
<b>CFC-11</b>	C-Cl <sub>3</sub> F	1.0	4000	137.5	7.8	24	0.88	None
<b>HCFC-141b</b>	CH <sub>3</sub> C-Cl <sub>2</sub> F	0.11	730	116.9	9.8	32	0.69	5.6-17.6
<b>HFC-134a</b>	CH <sub>2</sub> FCF <sub>3</sub>	0	1300	102.0	14.3	-26	5.62	None
<b>HFC-245fa</b>	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	0	820	134.0	12.2	15	1.24	None
<b>HFC-365mfc</b>	CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	0	840	148.0	10.6	40	0.47	3.5-9.0
<b>n-Pentane</b>	C <sub>5</sub> H <sub>12</sub>	0	11	72.0	14.6	36	0.65	1.4-8.3
<b>Iso-Pentane</b>	C <sub>5</sub> H <sub>12</sub>	0	11	72.0	13.8	28	0.80	1.4-7.6
<b>Cyclo-Pentane</b>	C <sub>5</sub> H <sub>10</sub>	0	11	70.0	12.6	50	0.34	1.4-7.8
<b>Carbondioxide</b>	CO <sub>2</sub>	0	1.0	44.0	16.3	-78	56.55	None
<b>Air</b>	N <sub>2</sub> /O <sub>2</sub>	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 HCFC 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

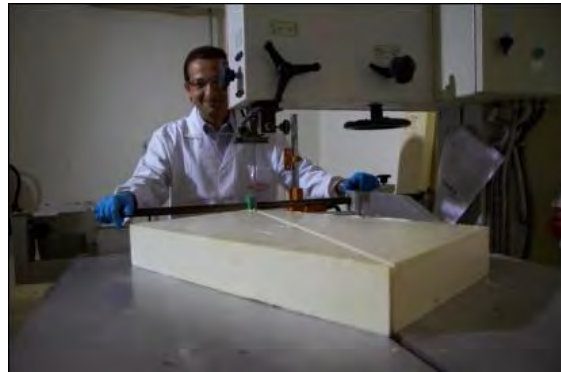




### **Mechanical properties: compressive strength**

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)**

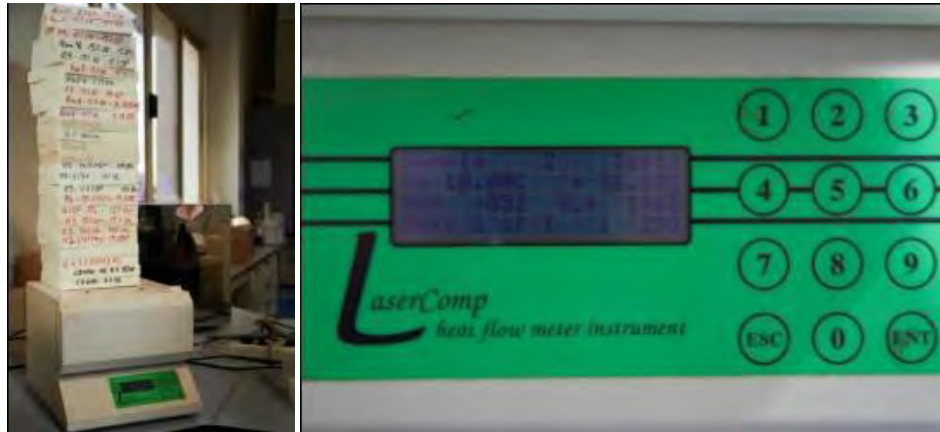
The test was performed according to EN 14509 (European product standard for sandwich panels) which refers to EN 1607.

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 blend 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
<b>HCFC141b</b> (pbw on top of 100pbw polyol blend)	18,7				
<b>c-pentane</b> (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.

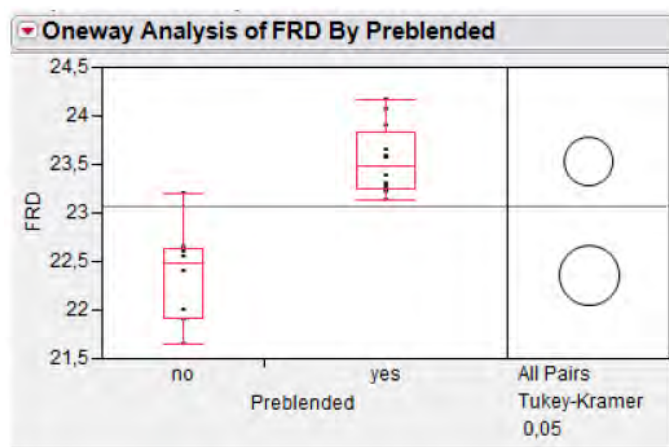


Chart 1: Free rise density comparative analysis third stream ( left) vs preblended (right)

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 blend 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/m <sup>3</sup> )	27,1	25,5	25,6	26,3
Minimum fill density MFD (kg/m <sup>3</sup> )	37,4	34,4	33,2	34,1
Applied density (kg/m <sup>3</sup> )	41,2	38	36,4	37,5
Average density distribution	0,85	0,59	0,3	0,44
Compressive strenght CS (kPa)	174	166	152	150
k-factor 10°C	20,1	21,2	22,4	22,2
Adhesion as TBS (kPa)	167	154	175	152
Dimensional Stability at +80°C (delta vol %)	<1%	<1%	<1%	<1%
Dimensional stability at -25°C (delta vol %)	<1%	<1%	<1%	<1%
Cycle time: post expansion % at 14' DMT ( on 100mm thickness)	5,0%	2%	0,5%	1,3%

Table 4: Extraction of data resulting from polyurethane foams for discontinuous panel applications produced with HP machine.

### Effect of type of addition: third stream vs pre-blended

For System C the general performance of third stream and pre-blended technology can be considered aligned between third stream and pre-blended pentane addition. All differences observed were in fact within the variability ranges of measurement methods used in the evaluation.

### N-pentane vs c-pentane comparison

This experiment exemplifies what reported in the literature and in this report introduction about the different performance of these two pentane isomers, confirming that n-pentane in general gives:

- improved flow properties which can lead to lower applied density
- improved mechanical properties and dimensional stability

- improved cycle time properties
- worse k-factor

Comparative with current HCFC141b technology in the market

Pentane based System D allows lower applied density compared to HCFC141b blown System C while keeping good foam properties (compressive strength, dimensional stability and adhesion to metal facings). Flow ability is slightly improved. Cycle time and process temperature latitude are improved when using pentane.

Only drawback observed with pentane based technology is the foam thermal conductivity: a 5-6% worsening was in fact observed with c-pentane and it was extended to 11% when using n-pentane.

**Systems for Water Heater application**

For water heaters a direct comparison of System E (HCFC141b blown) and F (HC blown )was performed. Only one level of pentane was run.

Table 5 reports main properties summary results from comparison of HC blown technology performance, both pre-blended and third stream addition option, vs HCFC 141b blown technology.

System	E	F	F
<b>HCFC141b</b> (pbw on top of 100pbw polyol blend)	19,5		
<b>c-pentane</b> (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-blend 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 in 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.

#### c-pentane preblended polyols physical and chemical stability

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 (c-pentane)	pentane content		physical stability	chemical stability	
	analytical ctrl			reactivity GT (sec)	free rise density (kg/m <sup>3</sup> )
	sample 1	sample 2	visual sample 1,2		
<b>Room T 23°C</b>					
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
<b>High T 50°C</b>					
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.

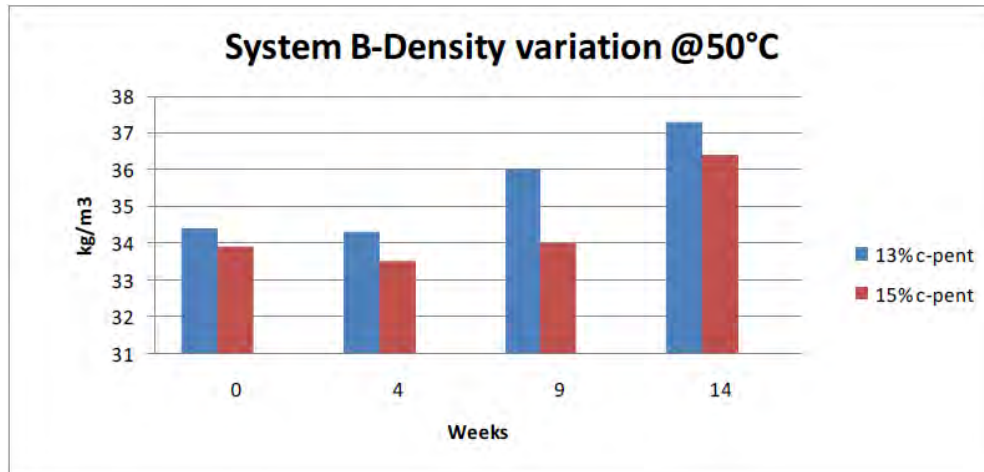


Chart 2: evolution of free rise density along time at 50°C aging temperature for polyol blend of System B fully formulated with c-pentane.

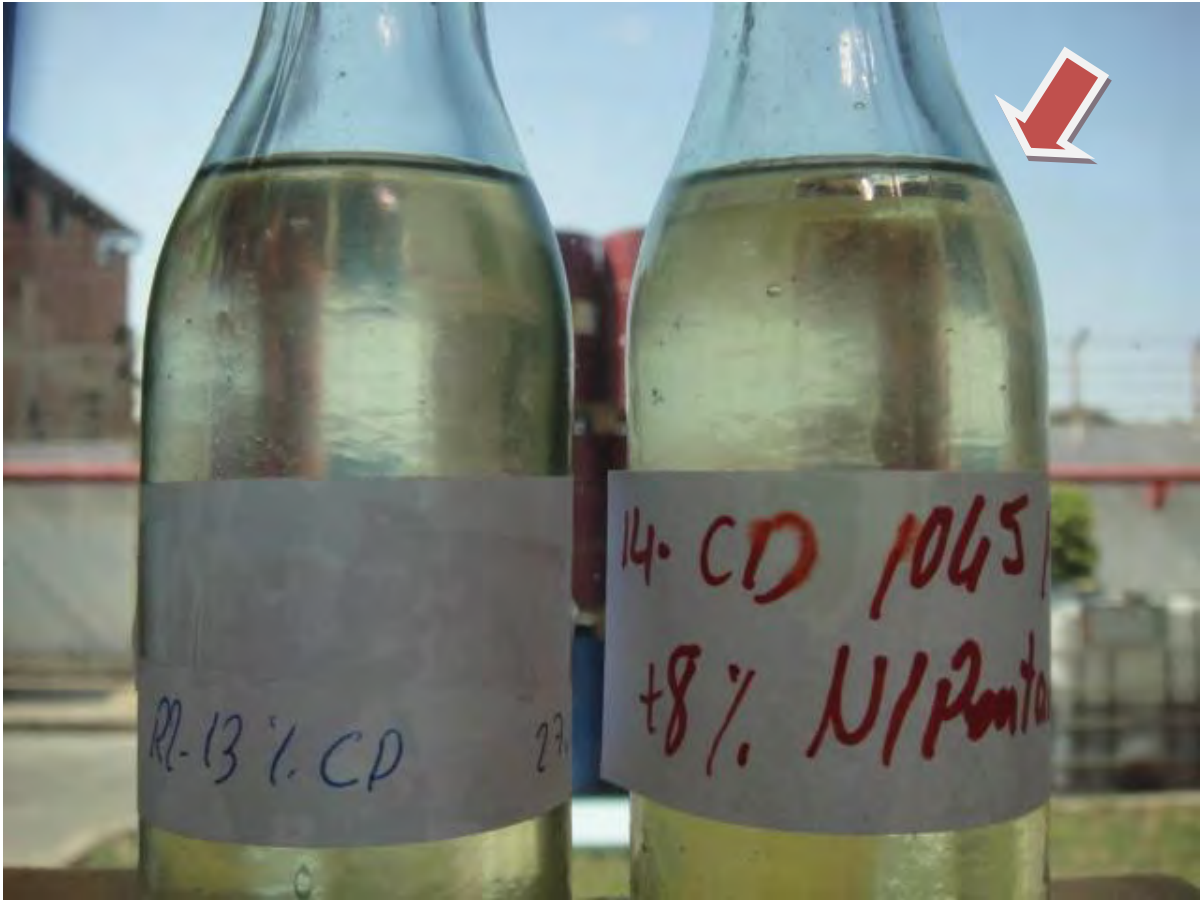
It is clear how the behavior of fully formulated blends would be not only formulation dependant but also handling and storing conditions highly dependent.

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.





## 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 HCFC 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.

## **Authors**

**Cecilia Girotti** is Sr. Chemist R&D for Polyurethane Rigid Foams of Dow Formulated Systems and is located in Correggio, Italy. She joined Dow in 2002 and before her current position she was responsible for managing the physic-mechanical foam testing laboratory in Correggio. Cecilia has a MS in Chemistry from the University of Modena (Italy, 1999).

**Francesca Pignagnoli** is Global Business Development Leader for DOW Energy Efficiency Formulated Systems and is located in Correggio, Italy. She joined DOW in 1997 and before her current position she was Global Development leader managing R&D group for Rigid Polyurethane Systems. Francesca has a MS in Organic Chemistry from the University of Parma (Italy, 1995).

**Mohammed El Fikky** is Technical and Sales Representative for DOW Energy Efficiency Formulated Systems and is located in Cairo, Egypt. He joined DOW in 1998 and before his current position he was responsible for the TS&D laboratory Supervisor, Mohamed has a B.Sc in Chemical Engineering from the Higher Technological Institute, 10th of Ramadan City (Egypt, 1996)

## **Acknowledgments**

A particular thank to Amr Badawi, DOW Cairo System House TS&D Laboratory Supervisor, and all the technical staff with him in Cairo that supported the project. As well, a particular thank to SAIP technical team and Cairo agent, who collaborated actively along various steps of the experimental program to allow DOW team to use the new SAIP machine in the best conditions, and to UNDP for allowing DOW team the use of the new SAIP dispenser under optimal conditions.

**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 in this particular scenario, the topic of investing to handle flammability aspects and risks of pentane would be extended to a larger number of players, as supplier would have to invest to handle pentane in its operation, and as polyol blends containing pentane have flash point and are flammable materials, with additional costs upstream in the value chain to be sustained by suppliers, and that would reflect into system price.

Nevertheless, in order to understand the criticality of such scenario, shelf life of pre-blended polyol with pentane was studied for a prolonged time period to understand criticality.

The experimental program for data generation encompassed two different applications:

- commercial appliance
- discontinuous panels

and different pentane isomers:

- cyclo pentane (typically used in commercial appliance applications)
- normal pentane (typically used in discontinuous panel applications)

**EXPERIMENTAL**

**Physical stability of the polyol blend**

The evaluation of the blowing agents' physical stability in fully formulated polyols was performed by studying the total blend stability at room temperature along time. After properly mixing the fully formulated polyol with the blowing agent, 200 grams (0.44 lb) of the blend were poured into a glass bottle (capacity: 0.09 gal, 350 ml), visually monitoring phase separation at regular intervals.

**Chemical stability of the polyol blend**

The chemical stability of the polyol blends was evaluated by storing the fully formulated blends at room temperature and at 50°C, and by performing reactivity and free rise density measurements after specific time intervals. Glass bottles containing the fully formulated polyols were stored inside thermostatic baths kept at constant temperature (20 and 50°C respectively) under a walk-in suction hood. In order to minimize loss of pentane during the whole study a different glass bottle (sample) was used for each performance evaluation.

**RESULTS AND DISCUSSION**

**System A: Cyclo-pentane based system for Commercial appliance**

5 months aging of fully formulated polyol of system A, containing 13pbw of c-pentane on top of 100pbw of polyol, gave good physical stability with no c-pentane separation observed, as reported in Table 1 below.

Table1: physical stability of system A at room temperature

Test #	Initial	two weeks	4 weeks	6 weeks	8 weeks	20 weeks
Physical stability	No phase Separation	No phase Separation	No phase Separation	No phase Separation	No phase Separation	No phase Separation

Within the 5 months so far evaluated the chemical stability is almost ok, both at room and high temperature with only small acceleration of reactivity, as explained in Table 2 below. The system density remains constant versus time at both storing conditions.

Table2: chemical stability of system A

Test #	Initial	two weeks		4 weeks		6 weeks		8 weeks		20 weeks	
		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/m <sup>3</sup> )	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: System A reactivity variation

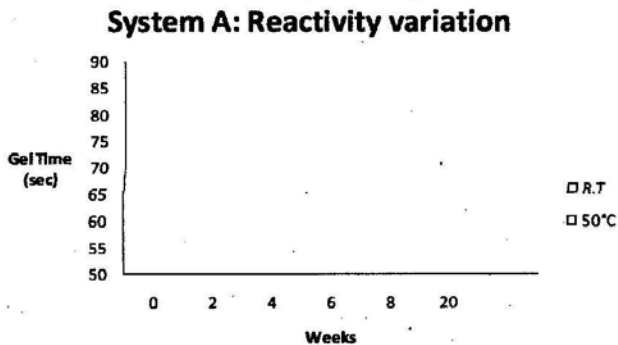
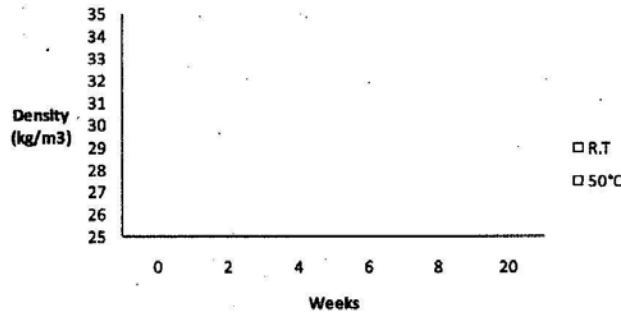


Figure 2: System A free rise density variation.

### System A: Density variation



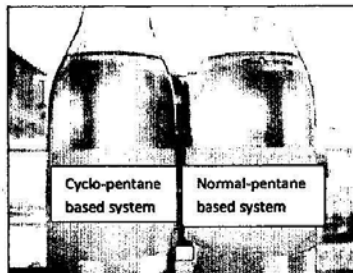
### System B: Normal-pentane based system for Commercial appliance

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°C a slightly density increase was observed already after 3 weeks.

Table4: chemical stability of system B

Test #	Initial	1 week		3 weeks	
		50 °C	Room Temp.	50 °C	Room Temp.
Reactivity (Gel time, sec)	125	ok	ok	ok	ok
Free Rise Density (kg/m <sup>3</sup> )	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.