



**Программа Организации
Объединенных Наций по
окружающей среде**

Distr.
GENERAL

UNEP/OzL.Pro/ExCom/76/58
20 April 2016

RUSSIAN
ORIGINAL: ENGLISH

ИСПОЛНИТЕЛЬНЫЙ КОМИТЕТ
МНОГОСТОРОННЕГО ФОНДА ДЛЯ
ОСУЩЕСТВЛЕНИЯ МОНРЕАЛЬСКОГО ПРОТОКОЛА
Семьдесят шестое совещание
Монреаль, 9-13 мая 2016 года

**РАСЧЕТ ДОПОЛНИТЕЛЬНЫХ КАПИТАЛЬНЫХ РАСХОДОВ И ДОПОЛНИТЕЛЬНЫХ
ЭКСПЛУАТАЦИОННЫХ РАСХОДОВ В ОТНОШЕНИИ АЛЬТЕРНАТИВ ДЛЯ СЕКТОРА
ПЕНОМАТЕРИАЛОВ (РЕШЕНИЕ 75/28).**

История вопроса

1. Представляя документ, в котором рассматриваются проблемы, выявленные в ходе анализа проекта¹, представленного 75-му совещанию, Секретариат пояснил, что при оценке некоторых этапов II ПОДПО невозможно было определить дополнительные эксплуатационные расходы (ДЭР) по смесям со сниженным содержанием гидрофторолефинов (ГФО) в секторе пеноматериалов². Неопределенность в отношении расходов была обусловлена главным образом тем, что неизвестно количество воды, добавляемой при совместном вспенивании с ГФО; каким образом меняется состав полиоловой смеси с учетом добавленной воды; количество полимерного метилendifенилдиизоцианата (МДИ), необходимого для смеси; а также отношение количества вспенивателя и полиола к МДИ. Небольшие изменения в допущениях при расчете ДЭР могут сильно повлиять на стоимость. Поэтому было предложено подготовить документ, посвященный расчету ДЭР для сектора пеноматериалов, для рассмотрения Исполнительным комитетом.

2. В ходе дискуссий на пленарных заседаниях и в учрежденной неформальной группе, участники выразили озабоченность по поводу того, достаточно ли зрелой является технология, много ли примеров ее использования и имеется ли достаточное количество пользователей для получения исчерпывающей информации. Было важно понять, в каких случаях приемлемо применение смесей со сниженным содержанием ГФО для вспенивания с водой, а также какой источник информации будет использован. Секретариат пояснил, что в основу предлагаемого документа будет положен обзор научной литературы и экспертное заключение независимого технического консультанта, для того чтобы представить Секретариату как можно более

¹ UNEP/OzL.Pro/ExCom/75/27.

² ГФО используется совместно с другим вспенивателем, главным образом с водой, для уменьшения стоимости полиоловых систем.

исчерпывающую информацию о расчете ДЭР для перехода на технологию с низким расходом ГФО, с разъяснением используемых коэффициентов.

3. В дополнение к дискуссии, Исполнительный комитет просил Секретариат подготовить документ для рассмотрения на 76-ом совещании, посвященный расчету дополнительных капитальных расходов (ДКР) и ДЭР по альтернативным технологиям в секторе пеноматериалов, обеспечивая прозрачность и последовательность при сравнении качества пеноматериалов, получаемых для разных целей, и прозрачность в отношении источников информации, с учетом цен в разных регионах и размеров предприятий (решение 75/28).

Техническое задание на подготовку документа

4. В ответ на решение 75/28 Секретариат выбрал независимого технического эксперта, который должен был подготовить документ о ДКР и ДЭР, связанных с переходом на не-ГХФУ альтернативы в секторе пеноматериалов, на основе технического задания, разработанного Секретариатом, которое, среди прочего, предусматривает описание:

- (a) оборудования, необходимого для производства пенополиуретанов (ППУ) (предназначенных для производства пеноизоляции электроприборов, исходных компонентов для изготовления панелей, цельных и составных панелей, распыляемых пен, блоков и интегральных пен) на основе ГХФУ-141b, и идентификацию изменений в оборудовании, и связанных с этим расходов, при переходе на альтернативные порообразователи (углеводород, метилформиат (МФ), метилаль, вода, ГФУ и ГФО);
- (b) типичных рецептов с ГХФУ-141b для основных типов ППУ и изменений, которые необходимо ввести в эти рецепты (включая суфрактанты, катализаторы, ингибиторы горения, стабилизаторы и другие добавки) для использования альтернативных вспенивателей;
- (c) рецептов, в которых другие порообразователи, главным образом вода, могут быть использованы совместно с основным вспенивателем (например, ГФО), их влияние на свойства пеноматериала (теплоизоляцию, хрупкость, размерную стабильность, плотность, прочность, компрессионную устойчивость, характеристики старения и отверждения и т. д.), и потенциальных издержек; и
- (d) объема необходимого тестирования, испытаний и обучения на всех предприятиях и связанных с этим расходов.

Рецензирование

5. Документ, подготовленный экспертом, был проанализирован двумя независимыми экспертами в области пеноматериалов, которые пришли к выводу, что рецензируемый ими документ является полным, фактологически правильным и понятным для человека, разбирающегося в технологии ППУ. Все замечания, сделанные рецензентами, были учтены экспертом в окончательном варианте документа.

Обсуждение на Межучрежденческом координационном совещании (МУКС)³

6. В ходе МУКС Секретариат обновил статус двусторонних учреждений и учреждений-исполнителей по подготовке этого документа и пояснил, что в решении 75/28 не указана роль учреждений-исполнителей в подготовке этого документа. Тем не менее, Секретариат приветствовал мнение учреждений-исполнителей и будет способствовать распространению этого документа среди учреждений, как только он будет завершен, отмечая, что в настоящий момент Секретариат не может уделить достаточное время рассмотрению комментариев учреждений.

7. После МУКС Секретариат представил окончательный вариант документа, подготовленного экспертом (с учтенными замечаниями рецензентов), учреждениям-исполнителям.

Замечания Секретариата

8. Секретариат отметил, что документ, подготовленный экспертом, соответствует техническому заданию, разработанному Секретариатом. Все комментарии и замечания двух рецензентов были на должном уровне отражены в окончательном варианте документа.

9. Основной темой документа является переход к альтернативным порообразователям, которые хорошо себя проявили с технической или коммерческой точки зрения и, следовательно, могут быть незамедлительно реализованы. Описаны типичные рецептуры для основных типов ППУ (в том числе для ППУ, предназначенных для пеноизоляции электроприборов, компонентов для изготовления панелей, цельных и составных панелей), а также соответствующие дополнительные расходы. Особое внимание было уделено новым проверенным технологиям с низким потенциалом глобального потепления на основе ГФО.

Выводы документа

10. Основные выводы документа, подготовленного экспертом, сводятся к следующему:

- (a) Каждый вспениватель, являющийся альтернативой ГХФУ-141b, имеет свой собственный набор уникальных физических свойств. Основные критерии выбора порообразователя включают коэффициент k^4 газа (или значение лямбда), растворимость в полиолах и давление пара. Ни один из вспенивателей не является идеальным замещающим (drop-in) агентом для ГХФУ-141b. Поэтому даже для самых простых вариантов конверсии требуется доработка рецептуры и проведение испытаний;
- (b) Более высокие изоляционные характеристики пеноматериалов, о чем свидетельствуют более низкий коэффициент k и улучшенные показатели энергетического испытания, наблюдаются при использовании ГФУ вместо ГХФУ-141b (улучшение на 4 процента). ГФО продемонстрировали еще более благоприятные результаты (улучшение на 10 процентов). Имеется теоретическая возможность уменьшить толщину пены, сохранив желаемый уровень изоляции. В результате этого снижение ДЭР будет значительным;
- (c) Легковоспламеняющиеся альтернативные агенты, такие как циклопентан и его смеси (например, с изо- и н-пентаном), хорошо зарекомендовали себя в

³ Межучрежденческое координационное совещание было проведено в Монреале с 1 до 2 марта 2016 года.

⁴ Коэффициент k является мерой тепла, проходящего через материал (измеряется в единицах Вт/мК). Он представляет собой коэффициент теплопроводности материала или способность проводить тепло. Обычно коэффициент k изоляционных материалов составляет менее единицы. Чем ниже коэффициент k , тем лучше изоляция.

производстве пеноматериалов для электроприборов, панелей и интегральных пен. Рецептуры, расходы на оборудование и методы применения для обеспечения безопасной работы хорошо известны и документированы;

- (d) ДКР на конверсию с ГХФУ-141b на пентаны высоки из-за высокой воспламеняемости пентанов. Потребность в оборудовании и цены сохраняются в течение последних 10 лет. ДЭР для материалов, вспениваемых с помощью пентана, являются минимальными, поскольку этот порообразователь, как правило, дешевле ГХФУ-141b и его расход ниже по сравнению с ГХФУ-141b. Таким образом, может быть достигнута значительная экономия ДЭР;
- (e) ДКР для ГФУ и ГФО являются минимальными, за исключением некоторых особых случаев. ГФУ-245fa и ГФО-1233zd дадут выигрыш от контроля температуры резервуаров или баллонов хранения полиоловых смесей в жарком климате (рекомендуются изолированные помещения с контролируемой температурой 20-25 °C для улучшения технологических характеристик ГФУ-245fa и повышения срока годности смесей ГФО-1233zd). ДЭР потребуются при переходе на ГФУ, поскольку ГФУ в 2,5-4 раза дороже ГХФУ-141b. Однако они позволяют получить эквивалентную или лучшую эффективность по сравнению с ГХФУ-141b (то есть пену с более низким коэффициентом k). ДЭР довольно высоки для пен, получаемых с помощью ГФО, главным образом из-за возросшей стоимости порообразователя. Однако их можно значительно снизить таким же образом, как для ГФУ: используя воду в качестве совспенивателя. Совместное вспенивание с водой, добавляемой в полиоловую смесь, значительно (на 0,5 – 2,5 процентов) снижает ДЭР, обеспечивая снижение расхода ГФУ или ГФО до 50 процентов. При использовании более 2,5 процентов воды свойства получаемого материала и технологический процесс резко ухудшаются. Максимально допустимое количество добавляемой к ГФО-1233zd воды составляет 2,0 процента от массы полиоловой смеси. Более высокий процент воды сокращает срок годности до менее чем 3-6 месяцев (т.е. ниже стандартного срока годности);
- (f) ДКР для пен, получаемых со 100-процентной водой, являются низкими и относятся главным образом к стоимости держателей пресс-форм, необходимых для создания более высокого давления, и (или) модернизации оборудования для нагрева и охлаждения пресс-форм для лучшего поверхностного отверждения и адгезии. При расчете ДЭР для пен, получаемых с использованием только воды, необходимо учитывать возможное увеличение плотности (до 10 процентов);
- (g) ДКР для МФ являются минимальными, по заявлению производителя, если закупать готовую полиоловую смесь и вспениватель. ДЭР являются низкими, применение МФ растет (а именно, с 400 метрических тонн (т) в 2009 году до приблизительно 2 000 т в 2013 году). Это увеличение объясняется его низкой стоимостью и приемлемыми характеристиками в таких изделиях, как цельные и составные панели, интегральная пена, электроприборы и распыляемые пены. Оптимизация рецептуры для применения в различных областях является критически важной для этого порообразователя из-за его высокой растворимости в полиоловых смесях;
- (h) Метилаль – огнеопасное вещество, но его можно использовать и обрабатывать так же, как углеводородные вспениватели. ДКР для метилаля будут такие же, как для углеводородов. Характеристики получаемого пеноматериала являются удовлетворительными для многих видов применения (то есть коэффициенты k как у циклопентана, но не настолько низкие, как у ГФУ или ГФО); и

- (i) Многие группы занимаются исследованием смесей пентана с ГФУ или ГФО для получения более низких коэффициентов k , чем у пен, полученных с использованием только циклопентана. ДКР эквивалентны расходам по переходу на 100-процентный пентан, а ДЭР зависит от количества ГФУ/ГФО, необходимого для достижения желаемого коэффициента k .

Использование воды в качестве вспенивателя

11. Одной из ключевых проблем, освещенных в документе, является использования воды в качестве порообразующего агента для жестких ППУ. Вода реагирует с изоцианатом с образованием газа CO_2 , который оказывается запертым в ячейках пеноматериала, обеспечивая его теплоизоляционные свойства. Как и у других вспенивателей, у этой альтернативы имеются преимущества и недостатки, которые кратко изложены далее:

- (a) Поскольку коэффициент k у CO_2 выше, чем у физических порообразователей, соответственно значение k пеноматериала также выше⁵ по сравнению с пенами, полученными с помощью углеводородов или ГФО. Кроме того, CO_2 будет мигрировать из ячеек и замещаться воздухом;
- (b) Вода обычно входит в состав систем на основе ГХФУ-141b для производства жестких ППУ низкой плотности, в количестве от 1 до 2% полиоловой смеси. Для получения жесткой пены методом вспенивания водой, требуется дополнительная вода (до 4,5 процента). Это количество воды будет поглощать примерно 70 частей полимерного МДИ. Расходы, связанные с этим дополнительным количеством полимерного МДИ, повлияют на стоимость смеси для производства ППУ;
- (c) Поскольку вода имеет низкий молекулярный вес, ей требуется большое количество изоцианата. Когда пена наносится с помощью оборудования для обеспечения фиксированного соотношения (1:1 по объему), это должно быть компенсировано выбором соответствующих полиолов с низким гидроксильным числом и, часто, включением нереактивных разбавителей (например, ингибитора горения или пластификатора);
- (d) Физические вспениватели обладают сольватирующим эффектом и использование вместо них воды приводит к увеличению вязкости полиоловой смеси. Этот недостаток можно компенсировать, используя альтернативные полиолы с пониженной вязкостью. Существует много таких полиолов; и
- (e) Недостатком пеноматериалов, вспениваемых водой, может быть их хрупкость. Для уменьшения хрупкости можно использовать ряд химических модификаций, в том числе снижение плотности сшивки полимера и введение большего числа блоков окиси этилена в молекулу полиуретана. Повысить адгезию можно с помощью катализаторов, которые селективно ускоряют процесс поверхностного отверждения.

Плотность пеноматериала

12. Другой ключевой вопрос, поднятый экспертом в документе: следует ли увеличивать плотность пеноматериала при переходе с ГХФУ-141b на альтернативный порообразователь. Такое увеличение требуется только для одного вспенивателя – 100-процентной воды. Увеличение

⁵ Чем выше значение k , тем хуже изоляционные свойства пеноматериала.

плотности используется для компенсации ухудшения размерной стабильности и компрессионной прочности. Другие рассмотренные порообразователи не требуют увеличения плотности.

13. Было высказано предположение о том, что увеличение плотности необходимо при переходе от ГХФУ-141b к циклопентану из-за более низкого давления пара в ячейках, что соответственно может ухудшить размерную стабильность. Увеличение плотности не требуется, поскольку размерная стабильность может обеспечена за счет правильной рецептуры. В частности, этого можно добиться увеличением плотности сшивок, например введением в рецептуру низкомолекулярных полиолов/полиолов с большим числом функциональных групп, таких как глицерин и полиол на основе сахарозы.

Комментарии, полученные от учреждений-исполнителей

14. На момент написания этого документа было получено несколько замечаний от учреждений-исполнителей. Они были рассмотрены вместе с экспертом и отражены в пересмотренном отчете, представленном в приложении I к настоящему документу.

Рекомендация Секретариата

15. Исполнительный комитет, возможно, пожелает:

- (a) принять к сведению документ, посвященный расчету дополнительных капитальных расходов и дополнительных эксплуатационных расходов по альтернативным технологиям в секторе пеноматериалов (решение 75/28), представленный в документе UNEP/OzL.Pro/ExCom/76/58; и
- (b) просить Секретариат об использовании технической информации, приведенной в документе UNEP/OzL.Pro/ExCom/76/58, при оценке дополнительных капитальных расходов и дополнительных эксплуатационных расходов, связанных с переходом с ГХФУ-141b на альтернативные порообразователи при производстве жесткого пенополиуретана.

Annex I

Blowing Agent Conversions from HCFC-141B to Alternatives in Article 5 Countries

March 2016

Tom Fishback, PhD

Blowing agent conversions from HCFC-141b to alternatives in Article 5 countries

Background

1. The Parties to the Montreal Protocol call for an accelerated phase-out of the use of HCFCs (decision XIX/6). Priority was given to the phase-out of HCFCs with higher ODP values like HCFC-141b, an ODS mostly used as a BA for the production of rigid polyurethane (PU) foam, and to a lesser extent as a solvent. In support to this decision, extensive analysis on the incremental capital and operating costs associated with the phase-out of HCFCs in the foam and refrigeration manufacturing sectors¹ had been conducted thorough assessment of alternative BAs, in particular methyl formate², methylal³, hydrocarbon-based preblended polyols⁴, super critical CO₂⁵, and HFO-1234ze⁶, as well as other reports.⁷

2. The objective of this study is to provide technical support for efforts aiding the development and implementation of HCFC phase-out management plans (HPMPs) in the rigid PU foam sector. The study is written from a technical basis grounded in the decision-making process common to the foam sector, based on commonly accepted rules, standards, practices, calculations, and commercial concerns. The study has benefited from the above-mentioned technical documents prepared under the Multilateral Fund, where information relevant to this study has been used and updated as required, as well as from several other technical reports related to formulations with different BAs. These concerns guide the presentation of material in this study.

3. The main topics addressed include the transition from HCFC-141b to alternative BA that have proven to be successful, either technically or commercially, which can be implemented immediately, or in very short order. Typical foam formulations by main application of interest (e.g., appliances, discontinuous and continuous panels, spray, block and pipe) are presented, as are their associated incremental costs. As an update from previous reports, special attention is focused on emerging, proven, low global warming potential (GWP) HFO (hydrofluoroolefin) options as well as the use of water as a co-BA.

Alternative BAs to HCFCs

4. The selection of alternative technology to CFC-11 as a foam BA⁸ was driven by the need to have a technology which would not only resemble CFC-based technology (virtual drop-in) but would also be

¹ Revised analysis of relevant cost considerations surrounding the financing of HCFC phase out (UNEP/OzL.Pro/ExCom/55/47).

² Methyl formate as BA in the manufacture of polyurethane foam systems: An assessment for the application in MLF projects, UNDP (UNEP/OzL.Pro/ExCom/62/9).

³ Methylal as BA in the manufacture of polyurethane foam systems: An assessment for the application in MLF projects, UNDP (UNEP/OzL.Pro/ExCom/66/17).

⁴ Low-cost options for the use of hydrocarbons in the manufacture of polyurethane foam: An assessment for the application in MLF projects, UNDP (UNEP/OzL.Pro/ExCom/66/17).

Conversion demonstration from HCFC-141b-based to cyclopentane-based pre-blended polyol in the manufacture of rigid polyurethane foam at Guangdong Wanhua Rongwei Polyurethane Co. Ltd, World Bank (UNEP/OzL.Pro/ExCom/66/17).

⁵ Supercritical CO₂ technology for polyurethane spray foam, Japan/UNDP (UNEP/OzL.Pro/ExCom/71/6/Add.1).

⁶ HFO-1234ze as BA in the manufacture of extruded polystyrene foam boardstock: An assessment for application in MLF projects (UNEP/OzL.Pro/ExCom/67/6).

⁷ The phase-out of HCFC-141b in rigid polyurethane insulating foams manufactured by small enterprises, World Bank (June 2014).

⁸ Blowing agents are gaseous, liquid or solid materials able to produce a foam structure. Physical BAs are those when the cells are formed through a change in the physical state of a substance (e.g., expansion of a compressed gas,

locally available to ensure access to technical support from systems houses and/or systems distributors. Depending on the products being manufactured, the production volume and the baseline equipment, several alternative technologies were chosen by Article 5 countries. Specifically, methylene chloride and liquid carbon dioxide technologies were selected for polyurethane flexible slabstock foam; water/carbon dioxide technology for flexible molded polyurethane; hydrocarbons (butane) for polystyrene and polyethylene foam and pentane (cyclo-, and/or iso-) for relatively large rigid and some integral skin foam operations.

5. For a large number of foam enterprises manufacturing rigid polyurethane and integral skin polyurethane foam enterprises, HCFC-141b met the needs of small- and medium-scale enterprises. HCFC-141b-based systems were technically mature and commercially available. They also provided relatively the most acceptable insulation value and energy efficiency, and the lowest investment and operating costs vis-à-vis other options. No major changes in the auxiliary equipment/tooling in the production programme, such as jig or mold redesign, were needed.

6. In light of the HCFC phase-out, Article 5 countries have or soon will phase-out their consumption of HCFC-141b for manufacturing foam. As in the case of the phase-out of CFC-11, an alternative BA for HCFC-141b is selected based on the maturity of the technology, its availability in the local market at acceptable pricings, and the critical properties of the end product, including thermal conductivity, dimensional stability and density.

7. Each BA candidate to replace HCFC-141b has its own unique inherent set of physical properties, which play a major role in influencing cured foam properties. For example, solubility of the BA in polyol blends is of extreme importance during processing.⁹ It is undesirable to have the BA separate from the polyol blend in day tanks, storage vessels (tanks, drums), and hose lines in processing equipment. Once a pre-blended polyol leaves a systems house it would be difficult to adequately remix the polyol blend at the mix head if BA has migrated into the head space. Mixing at the dispensing mix head of standard processing equipment (high or low pressure) should not be relied upon to “remix” separated chemicals. This is best done in the day tank or pre-feed storage vessel (drum, tote). Formulations are developed in every case to avoid separation of BA from the polyol blend before the mix head. Even 1 to 2% loss of BA into a head space region can noticeably affect foam quality.

8. Another property, gas k factor (or lambda value),¹⁰ is critical to the final insulating ability of the foam. For example, pentanes show higher gas k factors than HFCs and HFOs. These differences are apparent in the cured foam’s k factor, where pentane-blown foams show consistently higher k -factors. Other factors like conduction, convection, and radiative parameters also contribute to a foam’s ultimate thermal insulative capability. Improvement in these areas can be achieved through development of formulations with the finest cell structure possible.

9. A BA’s ability to maintain an adequate cell gas pressure in the cured foam is critical. BAs that condense into the liquid phase inside the cells of cured foam may experience shrinkage due to the reduced gas pressure within the cell. This reduced pressure can cause weak cells to pull inward, rupturing the cell struts, and thereby creating shrinkage.

or evaporation or dissolution of a liquid), while chemical BAs are those when the cells are formed by evolution of gases as thermal decomposition or chemical reaction products of a material.

⁹ The degree of foaming, cellular structure, and dimensional stability are all largely controlled by the solubility.

¹⁰ The k factor is the measure of heat that passes through a material (with units of W/mK). It represents the material’s thermal conductivity or ability to conduct heat. Usually, insulation materials have a k factor of less than one. The lower the k factor, the better the insulation.

Potential alternative HCFC-141b BAs

10. Potential HCFC-141b replacements for the main applications of interest considered in this report are listed below:

- Pentane isomers (cylo-, iso-, and n-)
- Water
- Methyl formate (MF), and possibly blends with pentanes
- Methylal
- HFC-245fa and HFC-365/HFC-227 blend
- HFO-1233zd and HFO-1336mmz
- Blends: pentanes/HFC, pentanes/HFO, HFC or HFO/water

Pentane isomers

11. Pentanes as foam BAs have been proven commercially in both non-Article 5 and Article 5 countries. Pentanes are five-carbon hydrocarbons obtained during refining/cracking of oil. They are physical BAs; have zero ODP and a relatively low GWP (maximum 25). The three main isomers of pentane used as a BA are:

- (a) Cyclopentane is a five-carbon closed ring structure. As a result of its “bulkiness”, it has the lowest k factor value of the pentane isomers, which in turn provides the highest ability to resist heat transfer through a cured foam, making it the best insulating gas of the pentanes. It is also the most expensive isomer;
- (b) n-pentane is a linear (straight-chain) five-carbon molecule. Not as “bulky” as cyclopentane in structure, it has a higher (worse) k factor value and a lower boiling point (36 °C); and
- (c) iso-pentane is a branched five-carbon molecule, with the lowest boiling point (28 °C) of the three pentane isomers, and with a k factor value (0.013 W/mK, @ 10⁰ C) similar to that of cyclopentane, making blends of the two isomers a good choice for thermal properties. Blends of iso-pentane and cyclopentane show improved solubility in polyol blends.

12. Currently, many appliance and panel manufacturing operations globally have adopted the use of cyclopentane and blends of pentanes. Cyclopentane-blown foam in appliances and panels provides the three most critical foam properties required: acceptable k factors, good dimensional stability, and adhesion to liners or panels. When used in integral skin applications, after vaporization and expansion of the foam, pentane formulations condense on the mold surfaces to help form “skins” on the surface of molded parts. Pentane formulations, however, have demonstrated limitations on achievable thermal properties due to their inherently higher gas k factors compared to HCFC-141b, HFCs, or HFOs. Additionally, the solubility of pentanes in polyol blends are less than other options like MF, HFCs, and HFOs, which makes them at times more difficult to process. Hydrocarbons cannot effectively be used in the growing market of spray foam due to their flammability.

13. Hydrocarbons have been the preferred conversion technology for large foam producers, where the safety requirements could be complied with and investments economically justified. Continuous boardstock manufacturers have shown a tendency towards n- and iso-pentane isomers in recent years for economic reasons. However, small-sized enterprises in non-Article 5 Parties have been unable to adopt

hydrocarbon technologies to any significant extent due to the investment need in new equipment.¹¹ Many SMEs that converted from HCFC-141 have selected HFC-based or HFO-based technologies despite the higher system costs. Where insulation requirements are less stringent, greater use of CO₂ (water) has also occurred.

14. Recent developments in equipment and technological processes appear to have made it possible for the investment costs as well as safety concerns associated with the technology to be considerably reduced. These developments would appear to make the conversion to hydrocarbon technology more affordable and feasible for enterprises with low- to medium-level of HCFC consumption. Furthermore, the role of systems houses in optimizing formulations for SMEs has been particularly important.

Water (water/CO₂)

15. Water reacts with MDI¹² to form CO₂, which then becomes the BA. CO₂ blown foam can have multiple inherent limitations in its cured state; higher densities (up to 10%) needed for dimensional stability, poor adhesion due to surface friability (poor surface cure) when applied to surfaces which are less than ambient temperatures (23 °C), poor flow in molds (discontinuous panels) resulting from high internal exothermic heats that cause early crosslinking, high polyol blend viscosities, and poor *k* factors.

16. The insulating capability of water blown foams reaches a limiting threshold because of the inherently low (compared with HCFC/HFC/HFO/MF) thermal insulating capabilities of the resultant BA gas trapped inside the foam cells. This gas is CO₂, initially, from the water/MDI reaction, but eventually changes to a high percentage of “air” through outward migration of CO₂ and inward migration of atmospheric nitrogen/oxygen. CO₂ has a GWP of 1.

17. Water is not a drop-in for HCFC-141b and requires extensive formulation optimization to create acceptable foams. Limitations on achievable final foam properties prevent water from being the unanimous choice for HCFC phase-out efforts.

18. Water-based systems became available in some Article 5 countries during the conversion from CFC-11 in rigid integral skin foams, rigid foams with relatively less critical insulation applications such as in-situ foams, surf boards, low density open-cell packaging foams, thermoware, and spray foam.

19. Water-based systems, particularly for rigid foams, are often more expensive than other HCFC-141b alternative technologies since the technology is associated with reductions in insulation value and lower cell stability. The problem is addressed by adding more material (up to 50 per cent) to increase foam thickness, where feasible, with resulting increase in cost. Thus, the use of water-based technology in pour-in-place for insulation applications, while in principle feasible, would require an increase in thickness, which is not always practical or cost-effective. In addition, the addition of water necessitates an increase in quantity of MDI in the formulation, which affects the operating costs.

20. Rigid integral skin foams have almost universally converted to all-water-based systems. In most of these applications, skin formation is triggered through densification (mold pressure) rather than condensation. Accordingly, subsequent coating may be required and densities can be increased. However, since densities in this application are already relatively high, this is not a major issue. This is not the case for flexible and semi-flexible integral skin foams. The related cost penalty arising from significantly increased densities and the poor skin formation associated with water blown systems has made the use of

¹¹ TEAP Progress Report, May 2008.

¹² MDI (diphenylmethane diisocyanate) is a versatile isocyanate that can be used to make flexible foams as well as semi-rigid and rigid polyurethane plastics.

pentane, hexane and HFCs attractive for flexible and semi-flexible integral skin foams in non-Article 5 countries and has caused almost universal conversion to HCFC-141b in Article 5 countries.

Methyl formate

21. Methyl formate, marketed by Foam Supplies Inc. (FSI) as Ecomate, is gaining acceptance in pour-in-place (mold filling) applications globally as time progresses. These applications include panels, appliances and marine boat filling (floatation). It is also being used in limited spray applications. Methyl formate is a physical BA; it has a zero ODP and relatively low GWP¹³ similar to other hydrocarbons.

22. MF is a flammable liquid in its neat state, but it can safely be used in polyol blends or as a third stream addition at the mix head. The lower flammability limit of these blends is well within safe use guidelines. MF is more soluble in polyol blends than HCFC-141b, which leads to a great need for formulation optimization.

23. Without sufficient optimization, issues that can occur with MF are excessive foam shrinkage (>5%) and poor adhesion. MF can effectively be used with water as a co-BA, further reducing its already relatively low cost compared to other BAs. *k* factors are acceptable. There are no significant regulatory issues with the use of MF.

Methylal

24. Methylal (dimethoxymethane) is a flammable liquid with a relatively low boiling point that belongs to the acetal family with good solubility in polyol blends. Methylal is miscible with all types of polyols commonly used in PU foam applications. Methylal-based non-insulation foams, regardless of application, match HCFC-141b foams while 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% (i.e., *k* factors are 10% higher (worse) than HCFC-141b).¹⁴ Due to its flammable nature, ICC for equipment are approximately US \$130,000 (only essential production equipment).

HFCs

25. HFCs have a higher insulating value (i.e., lower *k* factor) than other non-fluorinated foam blowing alternatives at operating temperatures for applications such as walk-in coolers and cold storage areas. To date, they have mainly been used where end-product fire performance is an issue with insurers or where investment costs for hydrocarbon-based technology are prohibitive, mainly for SMEs.

26. The three main HFCs currently used in foam applications are HFC-134a, HFC-245fa and HFC-365mfc (and its blend with HFC-227ea).

- (a) HFC-245fa (marketed primarily by Honeywell as Enovate 3000) is currently available across most, if not all, non-Article 5 countries. It is currently manufactured in the United States and China. It has been used to replace HCFCs in most rigid foam applications, including domestic refrigeration, spray foam, and metal faced sandwich panels. It has excellent flow properties, good solubility in polyol, foam density reductions and reduced panel waste due to ease of processing. In most cases it can be processed with the same

¹³ The supplier's claim of zero GWP is based on an evaluation from the U.S. Environmental Protection Agency Significant New Alternatives Program (SNAP), which described the GWP of methyl formate as 'likely to be negligible.' However, no actual was carried out to support this. Indeed, there is no chemical reason why the value should not be similar to that of other hydrocarbons.

¹⁴ UNDP, Methylal assessment, section 5.1 ICC, submitted to the 66th Executive Committee Meeting.

spray foam and pour in place dispensers used for HCFC-141b. HFC-245fa has zero ODP and a GWP of 1,020. HFC-245fa is typically used as co-BA with CO₂/water (from 0.5 to 2.5% of the polyol blend without reduction of critical properties) in order to gain from the thermal performance, while limiting the cost impact. If properly optimized in a formulation, water in the stated range provides a reduction in the HFC amount required, ranging from 10 to 20 parts of the polyol blend down to 5 to 10 parts in some formulations (i.e., about a 50% reduction in HFC). Some applications, such as discontinuous panels, have even shown that increased amounts of water in the 3 to 6% range result in acceptable foam when used with HFC-245fa. The amount of HFC-245fa was reduced to 5 to 7 parts in the polyol blend. However, a decrease in *k* factor (insulating capability) is noticed with these higher amounts of water, demonstrating well the trade-off in properties when using water as a co-BA with HFCs. HFC-245fa poses some technical challenges to formulators due to its low boiling point and its lower fire-resistance properties relative to HCFC-141b. It currently has limited commercial availability in Article 5 countries due to lack of demand. It has a high price, currently costing over US \$10/kg for bulk containers. Costs for HFC-245fa are expected to decrease in the coming years due to patent expirations. However, increased costs in certain regions may be observed due to marketing and supply issues.

- (b) HFC-365mfc and its blend HFC-365mfc/HFC227ea (marketed almost exclusively by Solvay Fluor as Solkane-365 and Solkane-365/227, respectively), is currently available in most, if not all, non-Article 5 countries. HFC-365mfc-blown foams have a fine cell structure with good insulation properties and good compressive strength. These foams are good for insulation purposes, where a non-flammable liquid foaming agent with low thermal conductivity is needed. However, HFC-365mfc has a lower blowing efficiency than some other alternatives. For several applications, HFC-365mfc is blended with HFC-227ea to overcome a minor flammability issue. It has also a high price in Article 5 countries, ranging from US \$12.00 – 14.00 /kg. HFC-365mfc has zero ODP and GWP of 610. HFC-227ea has a much higher GWP value (2,900), however, it is used in relatively small proportions;
- (c) HFC-134a has been used widely in Multilateral Fund projects as a refrigerant in refrigeration projects. However, its use as a foam BA has been very minimal due to processing difficulties, the fact that its pre-blends cannot be made available, and high production costs owing to the need for on-site pre-mixer which would limit its application by SMEs. Formulations with HFC-134a have been used to replace HCFCs in the manufacture of extruded polystyrene boards in North America. HFC-134a has zero ODP and GWP of 1,300.

HFOs

27. HFOs are now commercially available, and are sold in pure form to systems houses for making polyol blends. Honeywell (Solstice LBA, bulk) and Arkema (Forane HFO-1233zd, limited quantities) are the two HFO-1233zd suppliers. Chemours has announced the first production plant is scheduled to go online by mid-2017 for HFO-1336mzz.

28. HFOs have proven to be effective alternatives for HCFC-141b in a growing number of commercial foam applications (appliances, panels, spray), and represent the least climatically impactful BA solution for foams that require *k* factors better than or equal to HCFC-141b. HFOs possess the least impactful climatic properties (zero ODP, very low GWP, excellent foam *k* factors) for applications requiring the highest level of energy saving (insulation) performance. HFOs, like HFCs, are more

expensive than HCFC-141b, and this must be taken into account for IOC calculations. Costs relative to HCFC-141b are covered in the IOC section. Water is an effective co-BA with HFOs, decreasing the overall cost of polyol blends. The effective limit for high-insulation capability formulations is 2.5% in HFO-1336mzz, and 2.0% in HFO-1233zd. Water over 2% in HFO-1233zd can negatively affect polyol blend stability through interactions with catalysts and the BA. Addition of water can reduce the required HFO amounts by >50% in some cases. Although currently more expensive than HFCs, HFO costs are expected to come down somewhat over time as application adoption accelerates.

29. There are no significant safety concerns or capital requirements when converting from HCFC-141b. HFOs are a near drop-in for HFCs in insulating foams and have been used successfully in enough commercial applications and plant trials to encourage major regulatory agencies in non-Article 5 countries to draft regulatory steps for the phase-out of HFCs for foam blowing (2017 – 2021)¹⁵. However, special catalyst packages (more than one catalyst) are required for HFO-1233zd polyol formulations to achieve standard 3- 6 month polyol blend shelf lives.¹⁶ This results in a modest IOC impact detailed later in this study.

30. HFO-1336mzz is also a good substitute for HCFC-141b. It is inherently stable and compatible with standard foam catalysts. After initially announcing a 2016 production start, the manufacturer (Chemours) has now targeted its commercial availability for mid-2017, when the first production plant is scheduled to go online. It is also expected to be possibly more expensive than HFO-1233zd, necessitating formulation optimization efforts to minimize cost (though not requiring special catalyst packages).

HFC or HFO blends with pentanes

31. Blends of pentanes and HFCs or HFOs are emerging as a solution to stricter energy standards. A recent metal sandwich panel study showed that a HFC-365/n-pentane blend (30/70) gave a 9.4% lower foam core density and a 4.3% reduction in *k* factor (i.e., a 4.3% improvement in insulation) in comparison to the 100% n-pentane control. Appendix 3 includes the results of another panel study using different blends of HFO-1233zd and cyclopentane; *k* factors are significantly reduced. Improved energy efficiency standards are difficult if not impossible to achieve with cyclopentane alone, thus the drive for blends. This might be of particular relevance in Article 5 countries that export their manufactured goods to non-A5 countries where more stringent energy efficiency standards are prevalent, or if they have such standards themselves. Blends consisting of cyclopentane/HFO-1233zd or HFC-245fa have been found to effectively reduce foam *k* factors and improve processing characteristics, such as flow and density, over 100% pentane blends. MF blends with pentanes have also been applied in the field with good results.

Water as a co-BA

32. As previously noted, the insulating capability of water-blown foams is limited by the thermal insulating capability of the resultant BA gas trapped inside the foam cells. Water is, however, an excellent co-BA for insulating foams in amounts from 0.5 to 2.5% added to the polyol blend, where its positive impact on chemical costs are realized through an equivalent molar reduction (molecule for molecule) of the other, more expensive BA used. Water has a very low molecular weight (18), so an addition of just 2% represents a high number of BA molecules. Correspondingly, it is then possible to reduce the other

¹⁵ For example, the United States Environmental Protection Agency's (USEPA) draft ruling on this topic (June, 2014) will phase-out the use of HFCs in both domestic manufacturing and also imported products, an important distinction from the past where imports were allowed. Canada has indicated (2015) a willingness to follow closely USEPA and limit HFC uses. The European Union and Japan are similarly taking measures to limit HFC uses.

¹⁶ HFO-1233zd may react with the strong amine catalysts currently used in HCFC-141b foam formulations. Use of HFO-1233zd requires non-traditional catalyst packages consisting of less reactive amines and metal catalysts. It is possible that newer technologies will negate this issue in future years.

BA (e.g., HFCs or HFOs) by a similar or equivalent number of moles (molecules). The impact on reducing costs is always significant, sometimes reaching a >50% reduction in the more expensive BA. The negative effects of water on properties are not obvious, or are acceptable when used in this manner. As water reacts with MDI to produce the BA (in this case, CO₂), the addition of water necessitates an increase in the quantity of MDI in the formulation relative to a pure HFC or HFO-blown foam. This additional MDI in turn also affects the operating costs.

33. The general characteristics for each BA family as HCFC-141b replacement options are described in Table 1.

Table 1. HCFC-141b replacement BA characteristics

BA	Advantages	Disadvantages
HCFC-141b	<ul style="list-style-type: none"> • Low cost • High solubility, excellent processing • Low <i>k</i> factor • Non-flammable • Standard processing equipment 	<ul style="list-style-type: none"> • High ODP • High GWP • Subject to phase-out
Hydrocarbons (pentanes)	<ul style="list-style-type: none"> • No ODP or GWP concerns • Low cost • Acceptable solubility, processing • Acceptable <i>k</i> factor • Proven, mature technology 	<ul style="list-style-type: none"> • Flammable • High capital conversion costs so only applicable to higher volume usage • Not suitable for spray • Safety concern for SME hand mix
HFC-245fa; HFC-365/ HFC-227	<ul style="list-style-type: none"> • Zero ODP • Good solubility, processing • Equivalent <i>k</i> factors to HCFC-141b • Proven technology • Non-flammable 	<ul style="list-style-type: none"> • High GWP (>800) • High cost
Water	<ul style="list-style-type: none"> • Zero ODP • Low GWP • Non-flammable • Ultra-low cost • Excellent co-blowing option with HFCs, HFOs, and pentanes 	<ul style="list-style-type: none"> • Some processing challenges due to higher viscosity polyol blends • High <i>k</i> factor (i.e., poor insulation) • <i>k</i> factor decreases with time • Poor adhesion without heated molds, friability concerns • Density penalty ~ 10%
HFOs	<ul style="list-style-type: none"> • Zero ODP • Low GWP (<15) • Good solubility, excellent processing • Equivalent or lower <i>k</i> factors than HCFC-141b • Proven in some applications • Non-flammable 	<ul style="list-style-type: none"> • High cost (≥ HFCs) • Slightly higher catalyst amounts (cost) with HFO-1233zd
Hydrocarbon/ HFC or HFO blends	<ul style="list-style-type: none"> • Zero ODP • Low GWP in hydrocarbon/HFO blends • Reduced GWP in hydrocarbon/HFC blends • Same equipment as hydrocarbon • Lower <i>k</i> factors than hydrocarbon – helps meet stricter energy standards 	<ul style="list-style-type: none"> • IOC increase • ICCs high due to pentane
MF	<ul style="list-style-type: none"> • Not flammable in polyol blends • Excellent solubility, good processing • Acceptable <i>k</i> factors • Acceptable foam properties • Proven technology 	<ul style="list-style-type: none"> • Flammable as neat liquid • Requires rigorous formula optimization

BA	Advantages	Disadvantages
Methylal	<ul style="list-style-type: none"> • Low cost • Acceptable properties • Medium <i>k</i> factors • Some applications tested 	<ul style="list-style-type: none"> • Flammable as neat liquid • Capital conversion costs

Incremental costs for phasing out HCFC consumption in the foam sector

Ranges of incremental operating costs

34. The levels of incremental operating costs for conversion from HCFCs to non-ODS-based technologies depend mainly on the nature of the new formulations and the relative prices of chemicals used in those formulations. In addition, the density of the foam can substantially affect operating costs. In general, density is (inversely) related to yield per kilogram of the foam mixture. Enterprises generally seek to lower their operating costs by maximizing the yield per kilogram while maintaining key foam properties. Enterprises therefore seek to avoid increasing the density of foam when switching BAs. The exception to this is for water-blown foam, where an increase in density (up to 10%) is needed. Enterprises switching to the other BAs considered in this study would seek to use formulations that do not increase the foam density.

35. Raw material prices for PU foams change constantly according to global economic conditions, needs, and priorities. However, it is possible to pin down general ranges based on historical and current data. Low oil prices seen since mid-2015 will result in stable, relatively low prices for oil-derived PU raw materials such as MDI, polyols, and pentane BAs.

36. Fluorinated BAs (HFCs and HFOs) are not as dependent on oil prices and are expected to remain at current pricing levels until demand, capacity, and intellectual property situations change. For example, HFC-245fa prices should decline somewhat in 2016 and 2017 due to new producers taking advantage of expired patents. However, there may be small increases in the short-term due to commercial and marketing choices. HFO-1233zd prices should remain steady in 2016 and 2017. Supply and manufacturing capacity are not issues with HFO-1233zd. The story is different with HFO-1336mzz. To date, only research and development quantities from a pilot plant have been available for use in trials. There may have been a charge for some of this material, leading to a perception that it is currently available at a certain price. It is not commercially available in 2016. The production plant was originally scheduled to ramp up in late 2016, but according to the manufacturer (Chemours) that now has been pushed back to mid-2017. Regardless, HFO-1336mzz has shown that it has excellent foam blowing capabilities for when it becomes available.

37. The proportions of main chemical ingredients in foam formulations, namely the BA, the polyol and the isocyanate (or MDI) and their prices are the key determinants of the level of IOC. Prices of these main chemical ingredients have varied widely among Article 5 countries and continue to do so as shown in Table 2. This situation could result in substantial incremental operating costs for one enterprise but savings for another enterprise for the same type and amount of foam produced, depending on the prices of some or all of the ingredients, and the price differences before and after conversion. The use of relative foam system prices instead of the prices of individual chemicals where enterprises use premixed systems could help to mitigate some of the discrepancies in chemical prices.

Table 2. Price range of BAs in Article 5 regions

Chemical	Prices (US \$/kg)	
	Low	High
HCFC-141b	2.40	6.00

Chemical	Prices (US \$/kg)	
	Low	High
Cyclopentane	2.00	3.50
HFC-245fa	11.00	12.00
HFC-365/HFC-227	12.00	14.00
Methyl formate	3.00	4.00
HFO-1233zd	12.00	17.00
HFO-1336mzz	Unknown	Unknown

38. Table 3 shows the relative prices of raw materials and time required to develop formulations and achieve improvements on the properties of the foam in Article 5 regions.

Table 3. Relative formulation raw material costs and formulation development times in Article 5 regions

BA	Catalyst (\$↑or↓)	Surfactant (\$↑or↓)	Relative [^] BA cost	Relative [^] BA molecular weight	Polyols and/or MDI(\$↑or↓)
Pentanes	-	-	0.65	0.60	-
HFC-245fa	-	-	2.7	1.15	-
HFC-365/HFC-227	-	-	3.1	1.26-1.4	-
Water	-	-	-	0.15	↑ *
HFO-1233zd	↑ 2 – 3%	-	4	1.12	-
50% Reduced HFO-1233zd	↑ 2 – 3%	-	4	0.56	↑ **
HFO-1336mzz	-	-	≥4.00	1.40	-
50% Reduced HFO-1336mzz	-	-	≥4.00	0.70	↑ **
Methyl formate	-	-	0.8	0.51	-
Methylal	-	-	-	0.65	-

[^] relative to HCFC-141b

*quantity of MDI increases relative to HCFC-141b blown foam given reaction with water. Increase depends on formulation, desired density, and other factors.

**quantity of MDI increases given reaction with water. For every part water added, approximately 15 parts MDI is required.

39. IOCs in general are non-existent, minimal, or even negative when switching from HCFC-141b to pentanes and are low to moderate for methyl formate, methylal, and 100% water; possible density increases for 100% water-blown foam need to be taken into account. A significant amount of development work is currently being conducted on HFC or HFO blends with pentanes in larger A5 countries like China and India (see typical formulations section) to meet stricter energy standards in appliances and certain panel applications. Such blends, of course, would add IOC to the foam manufacturing operation, depending on the amount of HFC or HFO used. HCFC-141b transitions to HFCs or HFOs incur significant incremental operating costs.

40. The size of the enterprise can affect costs substantially. Small and micro enterprises should purchase pre-blended formulations from systems houses. Systems houses have the bulk purchasing power to obtain the lowest prices for BAs, particularly HFCs and HFOs, within a given region. Costs of these types of BAs can be extremely high if purchased in small quantities (5 – 50 kg cylinders) in A5 regions.

Costs for developing foam formulations

41. Each individual formulation within any foam sector has its own associated costs. Manufacturers typically use multiple formulations in production to produce goods according to their product line offerings. Individual formulators (chemists) in systems houses, or with large raw material/formulated systems suppliers, typically work on 1 to 3 formulations per 6 month period. Formulators need to spend considerable time optimizing a formulation when confronted with the need to develop new technologies of a significant nature, i.e., a total BA change. Table 4 shows typical formulation development and foam property improvement time frames.

Table 4. Formulation development times and trial/training costs

BA	Formulation time for chemist to change one formula (months)	Property improvement after launch (months)	Trials, training, technical support, materials, travel (US \$ per formulation)
Pentanes	3	3	10,000
Water	6	6 – 12	10,000
MF	6	6	10,000
Methylal	6	3 – 6	10,000
HFC-245fa	3 - 6	3 – 6	10,000
HFC 365/227	3 - 6	3 – 6	10,000
HFO-1233zd	3 – 6	3 – 6	10,000
HFO-1336mzz	3 - 6	3 – 6	10,000

42. Experience with CFC-11 and HCFC-141b phase-out in the foam sector has demonstrated the important role played by the chemicals suppliers and systems houses¹⁷ in tailoring the chemical systems¹⁸ used to manufacture foam to meet the needs of local markets and conditions. These intermediaries are capable of formulating foam systems to meet the specific needs of end-users.

Typical foam formulations in key applications

Appliances

43. Globally, most appliance manufacturers that have chosen alternatives to HCFC-141b use formulations blown with cyclopentane and pentane blends. Adoption of hydrocarbon-blown foams has occurred in Europe, Asia, Japan, and Article 5 countries. U.S. manufacturers have more often chosen HFC-245fa to replace HCFC-141b. Typical formulations are listed in Table 5 below along with critical foam properties; Table 5 shows a typical formulation where HCFC-141b is compared to HFO-1336mzz in a joint study by the BA manufacturer, a major polyol blend supplier, and a well-known appliance manufacturer. The results show improved *k* factors with the HFO over HCFC-141b. HCFC-141b and HFO-1336mzz were used on an equivalent molar basis.

Table 5. Typical appliance polyol blend formulation

Foam index	1.2
Mold temperature	45 – 50 °C
Polyol (sucrose/glycerine polyether polyols)	100 pbw
Catalyst	3
Surfactant	2
Other additives	4.9
HCFC-141b	15 - 30
H ₂ O	2 - 4

Table 5 (cont'd). Results using this formula for the study of resultant *k* factors

H ₂ O	3.8	1.7	3.8	1.7
HCFC-141b	16	30		
HFO-1336mzz			23	42
<i>k</i> factor @ 24 °C (mW/mK)	21.1	21.1	20.3	20.3

¹⁷ Systems houses are chemical companies that are engaged in the business of bulk pre-blending of foam systems for distribution and sale to foam manufacturers. The pre-blending obviates the need for investment in expensive in-house premixing stations and bulk purchase of several chemical components that are blended in the system.

¹⁸ Foam chemical systems are mixtures of chemical ingredients specially formulated and blended to meet specific foam processing conditions and product quality.

44. Table 6 shows foam *k* factor results from a study by a BA manufacturer and a major appliance manufacturer using a commercial appliance formulation. The results show an expected highest *k* factor (i.e., worst insulation) with cyclopentane, a HCFC-141b-equivalent *k* factor with HFC-245fa, and the lowest *k* factor (i.e., best insulation) with HFO-1233zd. As detailed in Appendix 3, studies have shown that blending cyclopentane with HFOs or HFCs improves the *k* factor (lower *k* factor and hence better insulation) relative to pure cyclopentane and pentane blends. Such blends will help meet more stringent energy requirements.

Table 6. Appliance foam *k* factors with different BAs

Blowing agent	<i>k</i> factor @ 24 °C (mW/mK)
Cyclopentane	21.0
HCFC-141b	18.5
HFC-245fa	18.5
HFO-1233zd	17.1

45. Critical foam properties for appliance foams:

- (a) The *k* factor is ultimately most critical because lower values generally correlate with results from energy tests on the appliance after manufacture. Energy saving requirements are becoming more stringent in developed countries where many A5 country finished goods are exported, as well as in the A5 countries themselves. HFCs and HFOs provide lower foam *k* factors (better insulating properties) than cyclopentane.
- (b) Density is related to yield per kilogram of the foam mixture. Therefore, it is critical for low operating costs that standard minimum fill densities are maintained.
- (c) Dimensional stability is critical for energy performance. If the foam shrinks it can pull away from the inner liner leaving voids lacking insulating foam.

46. Formulations:

- (a) Although they generally improve processing characteristics (over cyclopentane) such as flow, HFCs and HFOs exact a high cost penalty when used as a BA.
- (b) Cyclopentane offers the lowest cost choice when switching from HCFC-141b while still providing acceptable foam properties. High capital costs on the front end exist, but operating costs decrease due to the low cost of pentanes. Indeed, operating savings (relative to HCFC-141b) are common. Cyclopentane is inherently limited by its gas *k* factor with regards to improvements in current hydrocarbon-blown appliance energy test results.
- (c) Cyclopentane/HFC blends produce foams with better insulation properties (i.e., may provide an option for enterprises seeking to meet strict energy standards) but result in increased operating costs and the use of a high-GWP BA.
- (d) Cyclopentane/HFO blends produce foams with excellent insulation properties (i.e., may provide an option for enterprises seeking to achieve the best energy performance) and use only low-GWP BAs, but at present would result in slightly higher operating costs than cyclopentane/HFC blends.

47. Incremental costs:

- (a) HFCs and HFOs are $\geq 4x$ (Table 3) more expensive than HCFC-141b. The difference in the cost of the BA represents the only significant incremental operating cost when switching from HCFC-141b. HFCs and HFOs behave similarly to HCFC-141b in block and pipe foams.
- (b) Hydrocarbon-blown foam equipment costs (for safety) are well known and documented. The overall costs presented in Appendix I of UNEP/OzL.Pro/ExCom/55/47 continue to reflect capital conversion costs (ranging from US \$370,000-710,000 for retrofits and US\$385,000-780,000 for replacement). Other reports (e.g., Jeffs and Quintero, 2014) have corroborated those costs.
- (c) HFC/cyclopentane blends require the same equipment and precautions as 100% cyclopentane manufacturing.
- (d) Trial costs are typically \$10,000 per individual formulation (3 trials). These costs cover travel, material, and technical support/training.

Panels (continuous and discontinuous)

48. Aside from BAs during mandated transitions away from HCFCs, panel formulations tend to change the most with regards to the index (ratio of isocyanate to polyol reactive units, NCO/OH)). Polyurethane (PU) formulations in both discontinuous and continuous panels, have indexes from 1.2 – 1.5. PIR formulations (polyisocyanurate – contain ring structures formed from excess isocyanate) typically have indexes from 1.5 – 3.0. In a study by a major BA manufacturer, the resultant foam *k* factors for a typical polyurethane panel formulation are shown in Table 7. The data is consistent with other PU rigid foam applications in that the highest *k* factors come from cyclopentane, while HFC-245fa and HFO-1233zd provide values close to those of HCFC-141b.

Table 7. Typical Discontinuous Panel Formulation Panel Trial (discontinuous)

Components	php	HFO-1233zd	HFC-245fa	Cyclopentane	HCFC-141b
Polyether polyol	65				
Polyester polyol	35				
Catalyst	2				
Surfactant	1.5				
Flame retardant	22				
Water	2				
Blowing agent		23.3	24.0	12.5	21.0
pMDI (index ~ 1.2)	143.6				
<i>k</i> factor (@ 24 ⁰ C (mW/mK)		20.2	20.9	22.3	19.7

49. Larger enterprises can use hydrocarbon blowing technology to produce panels. As seen in all rigid insulating foam applications, blending hydrocarbons with HFCs and HFOs shows significant improvement in *k* factors (see Appendix 3).

50. Critical foam properties for panel foams:

- (a) *k* factor is the most critical property because lower *k* factors result in energy savings in end uses like walk-in coolers, etc.
 - (i) As with appliances, cyclopentane-blown foams perform adequately with regards

to energy, but possess limitations (cyclopentane gas k factor) with regards to achieving future improvements in energy performance.

- (ii) HFCs and HFOs provide lower k factors than cyclopentane.
- (b) Density is related to yield per kilogram of the foam mixture and therefore for low operating costs it is critical that standard minimum fill densities are maintained.
- (c) Dimensional stability is critical for energy performance. If foam shrinks it can pull away from the panel walls leaving voids lacking insulating foam and possible warping the panel surface. Adhesion to panel walls is critical in the same vein.

51. Formulations:

- (a) The choice of BA when switching from HCFC-141b will depend on the enterprise size and willingness to commit to the capital expenditures required for safe hydrocarbon foam processing. High capital costs on the front-end exist, but operating savings are possible due to the low cost of pentanes. Cyclopentane is inherently limited by its gas k factor with regards to improvements in current hydrocarbon-blown appliance energy test results.
- (b) HFCs and HFOs tend to lead to improved k factors but are more expensive than cyclopentane. They generally process better (flow) than 100% cyclopentane blown foams.
- (c) Cyclopentane/HFC and HFO blends result in improved k factors and therefore improved energy efficiency performance. Cyclopentane/HFO blends are likely to be slightly more expensive than cyclopentane/HFC blends but will likely result in lower k factors.
- (d) Methyl formate can be used for panels as a near-drop in for HCFC-141b. However, k factors are not as low as those seen with HFCs or HFOs (see Appendix 3).
- (e) Methylal has been used in panel formulations (see Appendix 4).

52. Incremental costs:

- (a) HFCs and HFOs are 4 - 6x (Table 3) more expensive than cyclopentane and cyclo/iso-pentane blends, and 2.7 - 4x more expensive than HCFC-141b. They represent the only significant IOC. However, they do not need to be used neat but can instead be used with hydrocarbons in polyol blends in the minimal concentration when required to meet stricter energy standards.
- (b) Hydrocarbon-blown foam equipment costs (for safety) are well known. Hydrocarbon has been the choice for major panel manufacturers, most of whom are quite large. Pentane blends with HFCs and HFOs require no additional capital costs beyond what is normal for pentanes, but costs can be expected for formulation trials and training.
- (c) Incremental capital costs for methyl formate are negligible other than trial costs if pre-blended material is used. For blending on site of flammable methyl formate and polyols, capital costs of approximately US \$130,000 can be expected.

- (d) Trial costs for any alternative panel BA system are typically \$10,000 per individual formulation (3 trials). These costs cover travel, material, and technical support/training.

Spray foam

53. Spray foam has experienced perhaps the fastest commercial growth of any global foam market sector since 2000. Spray foam is considered the ultimate building insulation because it is the only insulation material that combines the highest *k* factor per unit area with an ability to create a monolithic air seal around any substrate on which it is sprayed. The U.S. Department of Energy claims that stopping air movement through the building envelope can reduce heating and cooling costs by 40% annually. Buildings use more energy than any other application globally, and energy savings in this sector can result in a significant decrease of CO₂ emissions associated with heating and cooling. Table 8 shows a typical spray foam formula and the *k* factor of foam produced with that formula depending on the BA used (HCFC-141, HFC-245fa, and HFO-1233zd). The study was conducted by a major BA manufacturer.

Table 8. Typical Spray Foam Formulation and k-factors

Components	pbw
Mannich polyol*	40
Polyester polyol	60
Silicone	2
Catalysts	2.5**
Flame retardant	20
water	2
Index	130
BA	20***
<i>k</i> -factor (mW/mK) HCFC-141b	19.5
<i>k</i> -factor (mW/mK) HFC-245fa	19.9
<i>k</i> -factor (mW/mK) HFO-1233zd	18.7

*Mannich polyols contribute to a fast, even cure in spray foams and are used universally.

**5 - 6 for HFO-1233zd.

*** Less in some formulas.

54. Critical foam properties for spray foams:

- (a) Dimensional stability is critical for energy performance of the building envelop. If foam shrinks it can pull away from the framing or walls/roof decks, leaving gaps for air infiltration and exfiltration.
- (b) Density is related to yield per kilogram of the foam mixture and therefore to maintain the lowest operating costs it is critical that standard minimum densities (32 Kg/m³) are maintained. Foam densities > 38 kg/m³ begin to exhibit decreasing *k* factors.
- (c) Low *k* factors are critical because having the lowest *k* factor value among insulation choices, combined with spray foam's inherent monolithic (continuous) air barrier capability, justify its high cost in the market place.
- (d) Adhesion to substrates is critical for the same reasons as dimensional stability, but most problems arise from dirty or wet surfaces, not the foams.

55. Formulations

- (a) HFC-245fa and HFC-365/227, co-blown with water, are the BAs frequently used for spray foams in developed countries. They replaced HCFC-141b successfully.
- (b) HFO-1233zd is proven commercially in the United States, Canada and Europe. HFO-1336mzz has performed well in research and development trials. Both types of foams are normally co-blown with approximately 2% water.
- (c) Based on the success of HFOs, developed countries are in the process of developing fairly rapid regulatory phase-out schedules for HFCs in spray foams.
- (d) HFOs provide the lowest *k* factor (i.e., foam with the best insulation), have zero ODP and very low climate impact; however, they appear to be more expensive than HFCs.
- (e) HFO-1233zd cannot be used with many standard PU catalysts because of their strongly basic nature. Strong reacting tertiary amine catalysts may cause interactions with the carbon-carbon double bond of HFO-1233zd, leading to decay of polyol blend reactivity. Shelf stability of the polyol blend is greatly compromised in this case. A combination of slow reacting amines, sometimes in conjunction with metal catalysts (i.e., bismuth) has proven effective in providing standard polyol blend shelf lives of 3 – 6 months in drums.
- (f) Water can be used as the sole BA for closed cell spray foams. However, the foams have poor *k* factors relative to HFCs and HFOs ($\downarrow 30\%$), can exhibit excessive shrinkage, voids between foam and substrate, and poor process when spraying in cold temperatures (below 5⁰C).
- (g) Methyl formate can be used in spray foams with acceptable results. Work continues in this area.

56. Incremental costs:

- (a) HFCs and HFOs are 2.7 – 4x (Table 3) more expensive than HCFC-141b. They represent the only significant IOCs when switching from HCFC-141b. HFCs and HFOs behave similarly to 141b in spray foams and are fairly easy to transition.
- (b) HFOs are approximately 1.33x (Table 3) more expensive than HFCs, and are the only IOC in this type of transition.
- (c) Catalyst packages required for HFO-1233zd polyol blend stability typically utilize twice the amount of standard catalysts in this sector and add 2 -3% to the cost of the polyol blend.
- (d) Standard spraying equipment is used for all BA options.
- (e) For the best blend stability (shelf-life), it is recommended that polyol blends using HFO-1233zd not be exposed to high heat (> 30⁰C) for long periods of time during shipment or storage. A temperature-controlled insulated room for polyol blend day tanks or drums, along with similar shipping accommodations for drums is recommended for hot climates (US \$10,000-20,000 to insulate the room, US \$5,000 for an HVAC to maintain temperature).
- (f) Trial costs are typically \$10,000 per individual formulation (3 trials). These costs cover

travel, material, and technical support/training.

Block, Pipe

57. Block and pipe foams are rigid closed cell insulating foams designed to insulate irregular shapes. Block foams are cut into pieces which form-fit around various items that need to be insulated. Pipe foams are cut from blocks, injected between inner and outer pipes (pour-in-place), or applied to spinning pipes in OEM settings. A typical formulation is shown in Table 9.

Table 9. Typical Rigid Foam Insulation Formula (Block, Pipe)

Component	pbw
Polyol	65
Surfactant	2
Catalyst	3
Flame retardant	13
BA (HCFC-141b or HFC)	20*
Water (co-blowing)	2**
Index	1.1 (MDI/polyol blend)

*May be less depending on desired density, water co-blowing %, need for structural properties.

**4-6 if 100% water-blown.

58. Critical foam properties for block and pipe foams:

- (a) The *k* factor is ultimately most critical
- (b) Density is critical and needs to be 32–40 kg/m³
- (c) Dimensional stability is critical for energy performance. If foam shrinks it can pull away from the substrate leaving voids lacking insulating foam.
- (d) Compressive strength can be an important property since some of these types of foams are counted on to provide a measure of structural capability.

59. Formulations:

- (a) Methyl formate, water, hydrocarbons, HFC-245fa and HFC-365/227, and HFO-1233zd and HFO-1336mzz are all suitable as HCFC-141b replacements. The choice of BA simply depends on the requirements of the application (*k* factors, density, etc.).

60. Incremental costs:

- (a) HFCs and HFOs are 2.7 – 4x (Table 3) more expensive than 141b. They represent the only significant IOCs when switching from HCFC-141b. HFCs and HFOs behave similarly to HCFC-141b in block and pipe foams.
- (b) Processing equipment upgrades and retrofits should not be required when switching from HCFC-141b to any of the BAs above except hydrocarbon. HFC-245fa polyol blends may require cooling in hot climates (US \$10,000-20,000 to insulate a storage room and US \$5,000 for an HVAC unit to maintain temperature).
- (c) Mold costs may be incurred with the different BAs. Retrofits to molds for heating and cooling, or bracing for increased pressure (water blown,) cost between \$5,000 - \$25,000,

depending on the size and complexity of the mold. In addition, mold bracing may be needed (US \$1,000-3,000).

- (d) HCFC-141b to hydrocarbon would require capital investment as in all other cases for safety. Costs are well documented.
- (e) Trial costs are typically \$10,000 per individual formulation (3 trials). These costs cover travel, material, and technical support/training.

Integral-skin

61. Integral skin formulations vary significantly because of the wide variety of applications, such as office furniture, handlebar grips, automobile steering wheels, etc. Because of this complexity, a “base” formula will not be given in this report. In general, because of their higher densities, integral skin formulations they require far less BA than the typical rigid insulating foam formulations listed above.

62. The critical property for integral skin is the quality, hardness (look and feel), and thickness (durability) of the outer skin. Water, n-pentane, water/n-pentane, and methyl formate are typical alternatives to HCFC-141b. Safety-related costs associated with a conversion to n-pentane are prohibitive for small enterprises, but remain an option for medium to large enterprises. Methyl formate has shown good results in this application. In addition, the following observations can be made:

- (a) Skin quality rankings to date: n-pentane (excellent) > methyl formate (good) > water (poor to acceptable).
- (b) IOCs are negligible.
- (c) Mold costs may be incurred with the different BAs. Retrofits to molds for heating and cooling, or bracing for increased pressure (water blown,) cost between \$5,000 - \$25,000, depending on the size and complexity of the mold.
- (d) Trial costs are typically \$10,000 per individual formulation (3 trials). These costs cover travel, material, and technical support/training.

Ranges of incremental capital costs

63. The magnitude of incremental capital costs (ICCs) in the foam sector will depend mainly on the choice of technology. The ICC for conversion from HCFCs to non-ODS-based technologies depends on the enterprise’s existing baseline equipment; the type of foam products being manufactured and the volume of production; the alternative BA selected; and the location of the enterprise.

64. With the exception of hydrocarbons, ICCs are expected to be modest for enterprises that installed new equipment to convert from CFC-11 to HCFC-141b. Related costs needed by these enterprises to effectuate the conversion from HCFCs would mainly consist of technical assistance for training and the trial of new chemical formulations. Costs related to conversion of HCFC-based enterprises to hydrocarbon technology relate to the provision of new processing and safety equipment; however, the capability of small enterprises to absorb the hydrocarbon-based technology is likely to be limited.

65. Conversion to pentane-based technologies for foam enterprises usually requires high pressure dispensers suitable for use with hydrocarbon BAs, new polyol pre-mixers, hydrocarbon storage systems, and safety equipment to handle flammable substances. However, recent developments in the pre-blended

hydrocarbon-based technology and equipment design had the application of the technology more cost-effective for medium-scale foam producing enterprises.

66. For the conversion from HCFCs to HFC, HFOs, water-based systems or methyl formate technology no additional capital costs for replacing existing high pressure dispensers will be required by all the rigid polyurethane and integral skin foam enterprises. Costs related to technology transfer, training, trials and commissioning would be required to adapt the alternative technologies to local conditions. Capital cost for retrofit or replacement of existing baseline equipment, as well as technology transfer, training, trials and commissioning, might be required only for those enterprises that still process HCFC-141b foam with low pressure dispensers.

67. As a general matter, the decision of whether to use a high- or a low-pressure dispenser depends on factors other than selection of the BA. In particular, advantages of a low-pressure dispenser include:

- (a) Lower up-front costs
- (b) Ability to add 6 - 8 chemicals at the mix head
- (c) Lower mix-head throughput (i.e., less "splatter")
- (d) In general, better for thicker continuous panels because of this greater control
- (e) However, low-pressure dispensers tend to have **higher operating costs** as lines must be solvent-flushed after each foam pour.

68. In contrast, the advantages of a high-pressure dispenser include:

- (a) Higher throughputs
- (b) Faster cream times (reaction due to increased mixing energy)
- (c) Higher upfront costs
- (d) Lower operating costs (no solvent flushing as high-pressure dispensers are self-cleaning via a clean-out plunger)
- (e) Can only add 3 - 4 chemicals at the mix-head
- (f) Can splatter due to higher throughputs

69. The dominant factors used by enterprises in deciding whether to use a low- or a high-pressure dispenser are in bold, i.e., the factors that relate directly to cost: low-pressure dispensers are cheaper up-front but result in higher operating costs, while high-pressure dispensers necessitate a higher upfront capital investment but reduce operating costs. The choice of dispenser is also influenced by the needed throughput, control of line speed, and other factors.

70. The use of water as a co-BA with HFOs and HFCs can result in a small increase in viscosity of the polyol blend. Viscosity can be controlled, higher or lower, through;

- (a) Polyol selection (formulation adjustments)
- (b) Heats of processing (higher heat reduces viscosity, but then catalysis/rate of reaction

must be adjusted lower)

71. Thus converting from HCFC-141b to reduced HFO or HFCs does not automatically require a high-pressure dispenser.

72. Table 10 below provides a summary of the ICC ranges for various foam applications. These costs are based on enterprises with only one foam dispenser and auxiliary equipment in the baseline, and with HCFC-141b consumption of 5, 25 or 75 metric tonnes (mt) (or 0.6, 2.8 or 8.3 ODP tonnes) for manufacturing rigid foams, or 10 or 30 mt (or 1.1 or 3.3 ODP tonnes) for manufacturing integral skin foams. These levels of consumption represent typical small scale, medium scale and large scale operations. The minimum cost in the range has been based on retrofitting all required equipment items, while the maximum cost was based on the cost of replacing old equipment with new equipment, and represent the absolute levels. Costs of technology transfer, training and trials, which are a component of ICC, have been estimated on the amounts of chemicals needed to optimize foam formulations and are included. It should be noted that an additional \$15,000 – 20,000 (US \$) may be required for HFO 1233zd and HFC 245fa in very hot climates for cooling of BA/polyol blends during storage (cost not included in Table 10).

Table 10. Summary of incremental capital cost ranges for various foam applications (US \$)

Foam application	HFC-245fa/HFC-365mfc/ methyl formate/HFOs		Water-based systems		Pentane	
	Low	High	Low	High	Low	High
Panels and domestic and commercial refrigeration						
Retrofit	30,000	60,000			375,000	710,000
Replacement	100,000	195,000			385,000	780,000
Pipe in pipe and thermoware (*)						
Retrofit	30,000	60,000	25,000	55,000	375,000	710,000
Replacement	100,000	195,000	95,000	180,000	385,000	780,000
Spray foam (**)						
Retrofit	15,000	55,000	15,000	55,000		
Discontinuous block (box) foam (***)						
Retrofit	15,000	55,000	15,000	40,000		
Replacement	85,000	140,000	65,000	95,000		
Integral skin foam						
Retrofit	40,000	70,000	75,000	125,000	265,000	405,000

(*) Water-based systems would have limited application in pipe in pipe while pentane would have limited applications in thermoware.

(**) The flammability of pentanes would make their on-site application unacceptable.

(***) Box foam operation would make the use of pentane risky.

73. The decision of whether to replace or retrofit equipment is based in part on the age of the baseline equipment. Industry standards for the lifetime of equipment vary, including by the type of equipment. For example, storage tanks can last 10-30 years, while the lifetime of transfer pumps often varies between 5-10 years, and the electronic control panels for over 5 years, if properly maintained and serviced, and hoses are inspected and replaced if signs of wear or cracking are evident. The lifetime of mix heads depends on many factors, including regular servicing, annual foam throughput and number of total foam shots. Low pressure dispensers can last over 5 years and high pressure dispensers for a number of years, if properly maintained and serviced. Irrespective of maintenance and servicing, dispensers over 15 years old should be replaced rather than retrofitted.

Impact of lower *k* factors

74. As noted previously (see also Appendix 3), HFOs and HFCs give lower foam *k* factors than cyclopentane. The *k* factor reduction is approximately 10%. Given this, equivalent *k* factors to

hydrocarbon-blown foams can be obtained with HFCs or HFOs at equivalent foam densities in thinner parts, e.g., in panels. Some applications (certain appliances, spray foam in specific building code areas, and panels) can tolerate thinner parts/thicknesses and still meet industry thermal insulation standards. The relationship between foam k factor and foam thickness is not always linear, depending on formulation, processing, and sample preparation. For example, review of Engineering Service Test Reports (ESRs) for HFC-245fa blown spray foam show that k factors at the two standard thicknesses, 25mm and 87.5mm, are oftentimes different. In fact, manufacturer results are split; some are better at 3.5 inches than one inch, and some are worse.

75. More work must be done in establishing k factor – thickness relationships. For example, in a 100mm (thick) x 3000mm panel, a reduction of thickness of 12.5 mm gives a 12.5% decrease in the amount of foam required at equivalent densities to meet the same insulating performance. Savings can be significant. A 12.5% reduction in the amount of polyol blend at, for example 4.0 \$/kg, is a savings of \$0.5/kg. In this example, a 12.5% reduction in MDI would also be observed, contributing further to the savings.

76. In general, it is likely that there will be a learning curve as newer BAs such as HFOs are introduced and used in Article 5 countries. That learning curve will include formulation optimization for different applications, which will tend to reduce costs because of optimization of density and k factors, optimization for the particular application, or other factors. This was the experience with the transition from CFC-11 to HCFC-141b. Initially, there were substantial concerns with the transition. With experience, formulations were optimized and HCFC-141b gained broad acceptance as an effective BA. A similar experience is expected with the newer BAs.

Appendix 1: Blowing Agents and their Physical Properties

	Manufacturer	Trade name	Molecular weight	ODP	GWP	<i>k</i> factor (mW/mK)	Boiling point (°C)
HFC-141b			117	0.11	725	8.8	32
Cyclopentane			70	0	<25	11	49
n-pentane			72	0	<25	14	36
Iso-pentane			72	0	<25	13	28
HFC-245fa	Honeywell	Enovate	134	0	1,030	12.5	15.3
HFC-365	Solvay	Solkane	148	0	794*	10.6	40.2
CO ₂			44	0	1	16.8 @27 ⁰ C	-57 ⁰ C
HFO-1233zd	Honeywell Arkema	Solstice Forane	131	0	<15	10.6 @25 ⁰ C	19
HFO-1336mzz	Chemours	Formacel	164	0	<15	10.7	33
Methylal	Lambiotte & Cie		76	0	<15	14.5 @42 ⁰ C	42
Methyl formate	Foam Supplies Inc.	Ecomate	60	0	0	11 25 ⁰ C	32

*HFC 365 is always blended with 7% or 13% HFC 227 to make it non-flammable. HFC 227 has a GWP of 3,220.

Appendix 2: Chemical Descriptions of BA Families

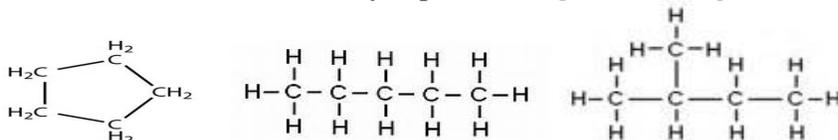
This section is a brief review of the chemical nature of the HCFC-141b-replacement BA families. Physical properties of BAs are listed in the Appendix 1.

Hydrocarbons

Pentanes (n-pentane, iso-pentane, cyclopentane) are five-carbon hydrocarbons obtained during refining/cracking of oil. They are physical BAs, meaning they “evaporate” as exothermic heat builds in the isocyanate/polyol mixture, expanding said material. The three useful isomers of pentane are described as follows:

- Cyclopentane is a 5-carbon closed ring structure. As a result of its “bulkiness”, it has the lowest lambda value of this group, which in turn provides the highest ability to resist heat transfer through a cured foam making it the best insulating gas of the pentanes. It is also the most expensive isomer.
- n-pentane is a linear (straight chain) five-carbon molecule. Not as “bulky” as cyclopentane in structure, it has a higher (worse) Lambda value and a lower boiling point (36⁰C).
- iso-pentane is a branched 5-carbon molecule. Its boiling point (28⁰C) is the lowest of the three main pentane isomers. In addition, its Lambda value (13 mW/mK, 10⁰ C) is close to that of cyclopentane, making blends of the two a good choice for thermal properties. Blends of iso-pentane and cyclopentane show improved solubility in polyol blends.

Pentane structures: cyclopentane, n-pentane, iso-pentane



HFCs

HFC 245fa, and HFC 365/227 are well-tested replacements for 141b. They are physical BAs. HFC 245fa is a carbon molecule with five fluorines. HFC 365 has 4 carbons and 5 fluorines. Both are linear in structure. Their structures contain no potential reactive sites for UV-induced degradation to occur in the atmosphere and therefore have GWPs > 800.

HFC structures

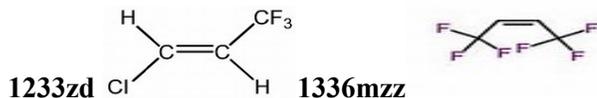


HFOs

HFOs are hydrofluoroolefins. Similar to HFCs, their structure is primarily carbons with attached fluorines. “Olefin” means that their structure contains a carbon-carbon double bond, site for attack by UV

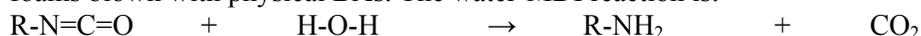
radiation in the upper atmosphere, which leads to their short atmospheric lifetimes and low GWPs (< 15). The chlorine-carbon double bond arrangement of 1233zd can lead to stability issues in polyol blends with standard amine catalysts (strongly reactive). Effective solutions for this exist.

HFO structures



Water (CO₂)

Water is a *reactive* BA. It reacts with isocyanate to form an amine (R-NH₂) and carbon dioxide. Carbon dioxide becomes the BA. The amine goes on to react with isocyanate (R—N=C=O) to form a polyurea rather than a urethane structure. This structural difference causes foam properties to differ at times from foams blown with physical BAs. The water-MDI reaction is:



Carbon dioxide has a vapor pressure of approximately 50 bar@20°C and thus is a very powerful foam expansion agent. An excess of isocyanate must be added to the combined foaming mixture in order to react with water to blow the foam. High exothermic heats from the water + isocyanate reaction make water blown foams difficult to control during processing and foam cure. Water's strong foam blowing capabilities, however, make it an effective cost-reducing aid in HFC, HFO, and cyclopentane blown formulations when used in the 0.5 – 2.5% by weight range in a polyol blends.

Methyl formate

Methyl formate (MF) is the methyl ester of formic acid. It is a physical BA. MF is highly soluble in polyol blends, which is an advantage in processing pour-in-place foams (improving flow), but can lead to issues like friability and poor dimensional stability if formulations are not rigorously optimized



Methylal

Methylal, or dimethoxy methane, is a colorless, volatile, flammable liquid with an odor resembling that of chloroform. It is often used as a solvent in adhesives and perfumes. It has been investigated as an alternative BA. It is a physical BA. Methylal is flammable, but it has been found that this can be controlled through blending with polyols. At this stage, methylal appears to be a promising co-blowing option in the future due to its ability to help solvate co-BAs into the polyol blend.

Methylal structure



Appendix 3: Summary of test results for different BAs for appliances, panels

Appliance studies

Table A3-1 shows foam *k* factor results from a study by a BA manufacturer and a major appliance manufacturer using a commercial appliance formulation. The results show an expected highest *k* factor (i.e., worst insulation) with cyclopentane, a HCFC-141b-equivalent *k* factor with HFC-245fa, and the lowest *k* factor (i.e., best insulation) with HFO-1233zd.

Table A3-1. Appliance foam *k* factors with different BAs

Blowing agent	<i>k</i> factor @ 24 °C (mW/mK)
Cyclopentane	21.0
HCFC-141b	18.5
HFC-245fa	18.5
HFO-1233zd	17.1

Table A3-2 shows relative *k* factors produced with HFO blends with cyclopentane in a commercial appliance formulation. The study was conducted by the BA manufacturer, a major polyol blend supplier, and a well-known appliance OEM using standard hydrocarbon/foam processing equipment. The addition of HFO reduced *k* factors, indicating that such blends will help meet more stringent energy requirements.

Table A3-2. *k* factors from a plant trial of HFO blends with cyclopentane

Blowing agent	Relative <i>k</i> factor @24°C (mW/mK)	Relative core density
Cyclo/isopentane	1.00	1.00
HFO-1336mzz/blend cyclo and isopentane	0.95	0.96
HFO-1336mzz	0.90	0.94

Table A3-3 shows data from a study by a major BA manufacturer using blends of cyclopentane and HFC-245fa and 100% HFO-1233zd in a typical formulation for appliance door and cabinet foaming, where each formulation was hand-mixed at 5,000 rpm then poured into a Brett mold. The lowest *k* factor (i.e., best insulation) was obtained by using 100% HFO-1233zd.

Table A3-3. Cyclopentane blends with HFC-245fa, HFO-1233zd

Blowing agent	Relative <i>k</i> factor @24°C (mW/mK)	Relative core density
Cyclopentane (100%)	1.00	1.00
Cyclopentane/HFC-245fa (60/40)	0.92	1.05
HFO-1233zd (100%)	0.89	0.98

Panel studies

Table A3-4 shows results from a panel trial conducted by a BA manufacturer using HFO/cyclopentane blends.

Table A3-4. Panel Trial Using 1233zd/Cyclopentane Blends

Blend: HFO-1233zd/cyclopentane	K factor (mW/mK)
0/100	22.3
25/75	22.0
50/50	20.8
75/25	20.5

Blend: HFO-1233zd/cyclopentane	K factor (mW/mK)
100/0	20.3

Table A3-5 shows the utility of methyl formate in panel foam. *k* factors are higher than with HFCs or HFOs, but the results are quite acceptable in some panel applications.

Table A3-5. MF 2014 panel trial India on HCFC-141b line (discontinuous)

BA	<i>k</i> factor* @24⁰C (mW/mK)
Methyl Formate	23.86