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Multilateral Fund
for the Implementation of the Montreal Protocol

METHYL FORMATE AS BLOWING AGENT IN THE MANUFACTURE OF POLYURETHANE FOAM SYSTEMS

Purcom Development Centre in the city of Barueri, Sao Paulo, Brazil. Courtesy of Purcom

Demonstration Projects on Alternative Technologies that Minimize Environmental Impacts

After the Montreal Protocol was adjusted in 2007 to accelerate the phase-out of HCFCs, Parties were encouraged to promote the development and the availability of alternatives to HCFCs that minimize environmental impacts, particularly for those specific applications where such alternatives are not presently available and applicable.

The decision of the Meeting of Parties to the Montreal Protocol (decision XIX/6, 2007) encourages Parties to promote the selection of alternatives to hydrochlorofluorocarbons (HCFCs) that minimize environmental impacts, in particular impacts on climate, as well as meeting other health, safety and economic considerations.

The Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol (Executive Committee) in its decision 55/43 has agreed on the importance of approving a limited number of projects in Article 5 countries to demonstrate emerging technologies in various industrial processes under local conditions.

Therefore, since 2007 the Executive Committee approved such demonstration projects in different sectors, mainly foam, refrigeration and air conditioning.

UNDP has been at the forefront of demonstration projects since 1992 and is implementing demonstration projects in all regions and all sectors. UNDP is assessing relatively new technological developments that have not or scarcely been used in developing countries. This task is conducted on behalf of and financed by the Multilateral Fund for the Implementation of the Montreal Protocol (MLF).

UNDP has been at the forefront of technology demonstration projects to replace ozone-depleting substances since 1992 and has been implementing demonstration projects in all regions and all sectors. UNDP is assessing relatively new technological developments that have not or scarcely been used in developing countries.

LOW CARBON TECHNOLOGY TRANSFER IN THE FOAM SECTOR

One of the challenges the foam producers are facing is how to convert the production technology to the one which would use the blowing agents with zero ozone depleting potential (ODP) and low global warming potential (GWP). This conversion would not only ensure that the countries are fulfilling their obligations under the Montreal Protocol but also lead to considerable reduction of greenhouse gas emissions thus mitigating the climate change

At the request of national counterparts and with financial support from the Multilateral Fund for the Implementation of the Montreal Protocol (MLF), UNDP has been implementing pilot projects in Brazil, China, Colombia, Egypt, Mexico and Turkey to assess the viability of different climate-friendlier alternatives to blowing agents used in the polyurethane (PU) and Extruded Polystyrene (XPS) production. As a result of these demonstration projects developing countries will be able to access the range of state-of-the-art and environmentally-friendly technologies tested under local conditions. For the PU foam and XPS sectors, assessments are being conducted for super-critical CO_2, methylal, optimized hydrocarbon technologies, CO_2 with methyl formate co-blowing and HFO-1234ze.

An assessment for the application of Methyl Formate as blowing agent in the manufacture of polyurethane systems

At its 56th meeting, the Executive Committee approved a demonstration project to assess the application of methyl formate (ecomate® as per trademark) as a blowing agent in the manufacture of polyurethane foam.

The use of methyl formate (MF) based systems in PU foams had the objective of assessing its performance compared with HCFC-141b based systems and establishing the feasibility of its use in MLF projects. The pilot project has been designed around Purcom Quimica LTDA, the largest independent system house in Brazil and specialized in tailor-made PU systems covering most PU applications. A notable exception is the application of PU foam in shoesoles, which has been validated through a pilot project executed by Quimiuretanos Zadro, a system house in Mexico that is specialized in PU shoesoles systems.

Methyl formate as blowing agent in PU foams was first introduced by Foam Supplies, Inc. (FSI). The company filed December 18, 2001 for a US patent which was awarded June 22, 2004. By now, FSI has filed for, or has been awarded, patents in most major countries. The develop-

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Injection test with a low pressure dispenser for validation of shoes soles formulation. Courtesy of Horacio Hernandez

ment of ecomate® has commenced in 2000, and under the name ecomate®, methyl formate was licensed to the following enterprises as of October 2010:

- Australian Urethane Systems (Asia Pacific)
- British Oxygen Corporation (selected European countries)
- Purcom Quimica (South America)
- Expanded Incorporation (India)
- Resichem(South Africa)

FSI has agreed to non-exclusive (sub) licensing to system houses that are beneficiaries of MLF-funded HCFC phase-out projects.

Project implementation

The project identified 17 polyurethane applications to test the use of methyl formate. After project approval in November 2008 a slightly modified action program was prepared based on:

- A thorough evaluation and incorporation in the assessment of previous work by FSI and its licensees; and
- Elimination of applications requiring direct injection (mostly continuous operations).

As a result the project assessed the demonstration of the use of methyl formate in 15 applications:

FLEXIBLE AND INTEGRAL SKIN FOAMS	RIGID FOAMS
Hyper-soft molded	Residential Appliances
Hyper-soft blocks	Other Appliances
Viscoelastic molded	Panels, Transportation, Reefers
Viscoelastic blocks	Spray
Steering wheels	Blocks
Structural (rigid)	Pipe-in-pipe
Semi-flexible	Buoyancies
Shoesoles	

Acceptability, for the purpose of this project, was defined as follows:

- Determining the safe use of the technology based on health, safety and environmental (HSE) data;
- Determining the applicability of the technology based on its processability;
- Determining the applicability of the technology by measuring relevant physical properties before and after replacing HCFC-141b; and
- Collecting complementary information from end-user enterprises that have tested MF formulations in their production lines.

Project Results

Health, Safety, Environment:

- The use of MF does not create health concerns up and above those with HCFC-141b. Both substances have flammable limits but in fully formulated systems it is unlikely that they may be reached under process conditions;
- Flammability of pure MF is an inherent safety risk and safety requirement must be met when dealing with pure MF. However, this risk is sharply mitigated — even virtually eliminated — at downstream user level when using fully formulated systems within the content limits;
- MF-based systems do not pose an environmental hazard based on current knowledge/regulations;
- MF-based systems are approved by the US EPA for use in all foam applications (SNAP approval).

System Processability

- Special considerations are required for the shipment and storage of pure MF;
- No special considerations are required for fully formulated systems with less than 6% MF (polyols) or less than 2% MF (MDI) following USDOT regulations. Local regulations have to be consulted;
- MF-blended polyol systems for all applications except for integral skin foams are stable. MF-blended isocyanate systems are always stable. The results do not support blending in isocyanate and proposes instead separate injection through a third stream as developed by Zadro for shoesoles;
- Although there is no conclusive evidence of corrosive effects, it is recommended that components that come in contact with pure MF or MF blends should be corrosion resistant;
- There are no identified compatibility issues of MF with polyols and/or additives. However, it is recommended that when designing conversion projects, the compatibility of baseline polyols will be carefully checked and any required changes to polyols and related costs should be identified.

Foam Properties

- MF based hypersoft and viscoelastic foams match HCFC-141b foams;
- MF based flexible/semi-/rigid/rigid ISF foams match HCFC-141b within 10% variation range;
- MF-based shoesole systems match or exceed HCFC-141b foams;
- MF based rigid foams for other appliances match HCFC-141b foams within 10% variation range;
- MF based spray foams match HCFC-141b systems within 10% variation range and outperform HCFC-134a and HCFC-22-based systems;

Integral Skin and Flexible Foam parts expanded with methyl formate. Courtesy of Purcom

- MF based rigid foams for discontinuous panels and transportation match HCFC-141b foams within 10% variation range;
- Product and long-term performance (reversed heat flow and 5 year performance) is also within 10% variation range and interested companies should analyze if this range is acceptable by their standards.

Dissemination of Results

Project results (excluding tests on the use for shoesoles) were presented and discussed during a workshop in March 2010 held in Curitiba, Brazil, with the participation of system houses, government officers, end users, national, regional and international experts, National Ozone Officers from the region and representatives from several implementing agencies as well as other providers of competing technologies. The completed assessment (also results on shoesoles applications) was presented at a workshop in Leon, Mexico in October 2010.

Complete report can be downloaded at ***http://www.undp.org/content/undp/en/home/librarypage/environment-energy/ozone_and_climate/Demoprojectsreport.html***

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CONCLUSION

Analysis of the outcome of the assessment led to the following conclusions:

- **The use of methyl formate as an alternative blowing agent to HCFC-141b in PU foam applications can be considered as an alternative in developing countries in flexible/integral skin foam applications and in a number of rigid foam applications. It is important to consider that for certain applications on rigid foam the technology could not be recommended at this stage and on others the application of the technology should be analyzed on a case by case basis and could be subject to further optimization;**
- **To minimize safety risks at downstream users, such projects should preferably be implemented through their system suppliers as fully formulated systems;**
- **Project designers should ensure that:**
  - **Chemical compatibility is verified;**
  - **Minimum packed density is observed;**
  - **Health, safety and environmental recommendations are incorporated;**
  - **Implications related to acidity are taken into account.**
- **In small and medium-sized enterprises its use was only recommended in preblended form via systems houses, in order to minimize the health and safety risks associated with handling such substances, and for specific applications.**

By the date of conclusion of the project in 2010, market penetration in most regions was very limited and the necessary infrastructure was expected to take one to two years to be put in place in many regions since methyl formate was not yet in use in most Article 5 countries. While the demonstration projects in two large Latin American countries had been successful, and investment projects funded by MLF are being implemented in Brazil, Mexico, Jamaica, Trinidad and Tobago and Dominican Republic, the application of methyl formate technology should be carefully evaluated in the context of the local situation prevailing in each country.