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Multilateral Fund
for the Implementation of the Montreal Protocol

METHYLAL AS BLOWING AGENT IN THE MANUFACTURE OF POLYURETHANE FOAM SYSTEMS

Arinos headquarters and production unit, city of Osasco, São Paulo, Brazil. Courtesy of Arinos

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 Methylal as blowing agent in the manufacture of polyurethane systems

At its 58th meeting, the Executive Committee approved a demonstration project to assess the application of methylal (ML) as a blowing agent in the manufacture of polyurethane foam.

UNDP formulated the project to investigate the safe use of methylal to replace HCFC-141b in polyurethane (PU) foams application. The use of methylal was first documented as co-blowing agent added to the cyclopenthane, mostly in Europe, being supplied by Lambiotte and Cie. In this sense, the pilot project aimed to evaluate the use of methylal as solely-blown based systems was evaluated at Arinos Quimica, Ltd. (Brazil), with the objective of assessing its performance compared with HCFC-141b based systems in order to establish whether the technology is feasible for use in Multilateral Fund projects.

To ensure that methylal technology would be available worldwide UNDP has first assessed the supply options and established that methylal is offered by manufacturers in Belgium, England, India, Korea and China. While methylal has been patented for a multitude of narrow PU applications, none of these patents cover broad use and/or have resulted in attempts to license its use and Lambiotte is of the understanding that that none of these patents could claim effective and comprehensive intellectual rights on the use of methylal in PU foams. Therefore it can be concluded that methylal is commonly available and free to use in foam applications.

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

Development and Certification Laboratory at Arinos Quimica, Ltd. Courtesy of Arinos

FOAM TYPE	APPLICATION		CRITICAL PROPERTIES	DEVELOPED AND TESTED
Non Insulating Foams	Integral skin foams	Flexible	Friability, surface	√
		Shoe soles	Surface	√
		Structural (rigid)	Surface	√
		Semi-flexible	Surface	√
	Flexible foams	Flexible molded	Appearance, touch	√
		Hyper-soft block	Appearance, touch	√
		Viscoelastic molded	Slow mechanical recovery	√
		Viscoelastic block	Slow mechanical recovery	√
	Semi-rigid foams	Packaging foam	Shock absorption	√
Insulating Foams	Rigid PU/PIR foams	Refrigeration	Insulation, adhesion, dimensional stability, (lack of) water permeability	√
		Water heaters		
		Trucks		
		Blocks, Panels		
		Spray		
		Thermoware		
		PIR Blocks		

Project Implementation

The assessment of methylal in PU applications addressed the following: health, safety and environmental considerations; issues concerning its processability (e.g., stability, compatibility shipping and storage); system composition; an overview of the physical properties obtained from trials for different applications; and indicative costs of conversion for introduction of the technology in systems houses and foam enterprises.

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

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

Implementation started with a review of the potential to combine applications based on same or very similar formulations, determination of the assessment parameters and critical issues for acceptability. The applications template was then functionally rearranged as shown in the table above.

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

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

Project Results

Health, Safety, Environment:

- Methylal does not create incremental health concerns;
- Methylal does not pose an environmental hazard;
- Methylal shipments and storage in its pure form must comply with its flammability status;
- While on downstream level, safety concerns may be mitigated through preblending, methylal still requires safety measures
    - In fully formulated systems <2% methylal (polyols) or <2% the use of methylal (isocyanates) requires no special safety considerations;
    - Systems containing 2-5 php methylal need individual consideration and above that level, compliance with the Globally Harmonized System (GHS) category 2 or 3 is required;
    - Local regulations are also to be complied with.

System Processability

- Methylal is stable in fully formulated systems for all applications;

Methylal workshop.

- Its use in blends is not corrosive;
- In blends with polyols and/or additives methylal does not pose compatibility issues. However, when designing conversion projects, it is recommended to carefully check the compatibility of baseline polyols and determine the impact on flammability characteristics;
- The shelf life for methylal is at least 6 months under standardized conditions.

Foam Properties

- In non-insulation foams, regardless of application, methylal matches HCFC-141b foams;
- In thermal insulation foams methylal matches HCFC-141b foams within a range less than 10% of variation in stability and density but carry a penalty in insulation value of up to 10 %. This range is comparable with methyl formate and better than hydrocarbons and water-based systems in front of HCFC-141b based foams;
- All customers selected for performance trials — one per application —expressed their agreement with the performance of methylal-based PU systems;
- Conversion cost estimates show low capital and operating costs. It should be pointed out, however, that these costs can differ significantly from country to country and based on comparative size; and
- No data on long-term performance are yet available.

Dissemination of Results

The pilot project for the evaluation/assessment of methylal included a workshop to disseminate the results of the project, which was held in Brazil in December 2011. Over one hundred participants from Belgium, Brazil, Colombia, Jamaica, Panama, Paraguay, and Peru took part at the workshop.

CONCLUSION

As a result of the project, it can be concluded that methylal can serve as a feasible alternative blowing agent to replace HCFC-141b in PU foam applications. However, no data on long-term performance are as of yet available. The final project report also provided recommendations for setting up the technological process of using methylal as a blowing agent to ensure safety and environmental considerations. The use of methylal instead of HCFC-141b will have significant positive impact on climate: methylal's GWP is negligible compared to GWP of 725 of HCFC-141b (IPCC Fourth Assessment Report, 2007). The project also considered costs of conversion and found them to be similar to the use of HCFC-141b. However the costs will depend on the local economic and market conditions.

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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