

AN UPDATE ON THE DEVELOPMENT OF TIF MULCHING FILMS

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We initially introduced TIF™ or “totally impermeable film” technology, based on the use of high barrier EVAL™ ethylene vinyl alcohol copolymer (EVOH), at MBAO in 2007. TIF offers both extremely low fumigant vapor permeation and excellent film handling properties suitable for tractor application in narrow row mulch or wide broadcast fumigation. An early, yet-unpublished, highlight of the research conducted by Dr. Husein Ajwa of UC Davis in 2007 was that TIF reduced drip-applied chloropicrin peak and total emissions by about 85% compared to standard HDPE film. The advantages on fumigant vapor barrier of TIF versus VIF and standard tarp technologies versus various fumigants can be summarized in the table below.

Transmission Rates at 20°C (µg/m ² .hr) **				
Technology	TIF 1	TIF 2	VIF	PE
Grade	EVAL H171	EVAL SP292	Nylon 6	LDPE
Methyl bromide	< 0.0001	0.0004	47	235
Methyl iodide	< 0.0001	0.0002	33	330
Chloropicrin	0.0451	0.183	120	384
Cis 1,3-dichloropropene	0.129	0.428	173	393
Trans 1,3-dichloropropene	0.127	0.479	36	298

Testing conducted by the University of California Davis, Plant Sciences Department (Nov 2007)

Film structure tested: LLDPE / Adhesive / **Barrier*** / Adhesive / LLDPE = 15 / 3 / **4** / 3 / 15 µm

TIF1 and TIF2 have different grades of EVAL

*LDPE sample was a 40µm monolayer film with low density polyethylene (1.0 g/10min MI, 0.90 g/cc density)

Ny 6,66: Polyamide 6,66 copolymer

In July 2008, the USEPA released its final iteration of the Re-registration Eligibility Decisions (REDs) for both methyl bromide and chloropicrin, as well as for the MITC generators. In this document, the USEPA approved buffer zone reduction credits for a type of TIF (referred to as “EVAL/Mitsui film”) of 25% and 40% for methyl bromide and chloropicrin, respectively. In May 2009, the USEPA released the Amended REDs, where TIF with EVAL EVOH was approved for a 60% buffer zone credit for both methyl bromide and chloropicrin based on UC Davis film permeability testing of TIF that had been put through the rigors of field application using standard industry practices and equipment.

In addition to tests conducted under lab conditions, Kuraray is participating in three regional (CA Central Valley, CA Coast, and FL) large-scale field volatility (“emissions” or “flux”) studies that are ongoing in 2009-2010. One objective of the studies is to provide new emissions data to the USEPA for a revised risk assessment (affecting buffer zones and related mitigation measures). The other objective is provide new emissions data to the CAL-EPA (CDPR) for consideration of VOC emission reduction credits and the CDPR-enforced buffer zones, which differ from those proposed by the USEPA. The

data should also validate both the TIF lab test results and the USEPA buffer zone reduction credit given for TIF.

The first study was conducted in Wasco, CA, in June 2009. It evaluated emissions from five fields, each using a different application method but where all were treated with 350 lbs/acre of MB/PIC 50/50. Three fields were treated with the shallow (12-inch injection depth) broadcast tarp method that will allow comparisons between standard tarp, TIF, and TIF with a potassium thiosulfate (“KTS”) spray. KTS is a fertilizer known to degrade halogenated compounds like methyl bromide and chloropicrin; and is categorized as a “reactive boundary layer” that may also receive a buffer zone reduction credit in the USEPA regulations. The other two fields were deep (18-inch injection depth) tarped, both utilizing TIF, where one field was broadcast and the other was done as tarped strip. The strip treated field consisted of alternating runs of tarped (fumigated) passes and non-tarped (not fumigated) passes. These data are in progress. The study was conducted by Dr. Husein Ajwa and Mr. David Sullivan, and funded by the USDA, the Methyl Bromide Industry Panel, and Kuraray. TriCal was the applicator for all study fields.

Additional research in 2009 has focused on the fumigant dose response (application rate reduction potential) of TIF. Numerous trials in both the Western and Eastern US on a variety of crops have been done or are pending in collaboration with UC Davis, USDA/ARS, TriCal, Hendrix & Dail, and Raven Industries. One such trial already underway at the USDA/ARS research farm in Salinas involves Albion strawberries and is being supervised by Dr. Steve Fennimore of UC Davis. Rate reduction potential is being evaluated with treatments of 400, 300, 200, 100 and 50 lbs/acre of Pic-Clor60 (55.6% chloropicrin + 33% 1,3-dichloropropane) compared to a control dose of 350 lb/acre MBPic. Preliminary fruit yield, plant vigor and weed density data demonstrate that rate reductions under TIF are promising.

Mulch films due to their very thin nature must meet demanding mechanical property requirements to have good fit-for-use characteristics for field application. The use of unique EVAL EVOH resins, the proper selection of complementary polymers, the design of the multilayer structure, and proper film processing techniques give TIF the right balance of fumigant vapor barrier and mechanical properties to meet the challenge. A well known advantage of EVAL EVOH over Nylon resins is the significantly lower diffusion of gases through the polymer. This fact allows converters to run a barrier layer that is thin enough for the film to have good mechanical properties while meeting the permeation requirements to qualify for the USEPA mandated 60% buffer zone credits for methyl bromide and chloropicrin. In addition to mulch fumigation films, there are commercial applications for silage films and initial research for anaerobic soil disinfestation where TIF is being used for its high barrier properties to oxygen.

The gas barrier property of EVAL EVOH is imparted by its molecular structure and semi-crystalline morphology. The crystalline region is highly ordered in nature and essentially impervious to the diffusion of gases. The amorphous region of EVAL EVOH, although highly disordered, benefits from hydrogen bonding forces, polar forces and dipole-dipole forces that result in amorphous regions with low free volume space.

An important point for film producers to consider is that the resulting crystallinity of EVOH can be influenced by processing factors such as orientation and cooling rate. For example, because blown films are cooled slowly and undergo biaxial melt orientation they tend to have a higher degree of crystallinity than cast films which are quickly chilled and mono-axially oriented. Rapid cooling hinders the growth of crystalline domains in the initially fully amorphous matrix in the molten state. The difference in the mode of orientation affects the balance of mechanical properties in the machine and transverse direction in which the film is produced. Balanced properties are desired to prevent tearing of the film particularly when being used in raised bed fumigation. With that said, structure and output being constant, a layer of EVAL EVOH produced in a blown film process will have a higher crystallinity and higher fumigant barrier than a layer of EVAL EVOH produced in a cast film process.

In addition to understanding the basic properties of EVAL EVOH, Kuraray has the technical resources and has developed a unique EVAL EVOH technology to assist film manufacturers in the development of the right TIF structure with the proper balance of mechanical and barrier properties for thin tough, thin mulch films.

Kuraray America, Inc. has been marketing EVOH under the EVAL trade name into different markets for over three decades. Current markets served include food packaging, automotive fuel components, and industrial chemical packaging. EVAL EVOH is used in food packaging for its excellent oxygen barrier; in the automotive market for the containment of hydrocarbon vapor in fuel systems; and in industrial chemical packaging for its excellent resistance to hydrocarbons.