



 **EVAL**

AGRICULTURAL APPLICATIONS



kuraray



EVAL™

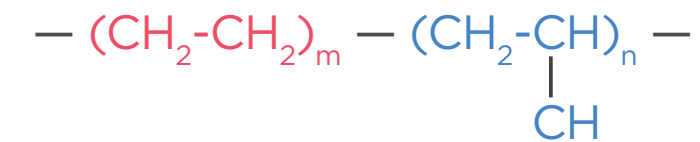
EVAL in Fumigation Films

Kuraray Co., Ltd is the world leader in the production of EVOH (ethylene vinyl-alcohol copolymer) resins. Kuraray markets its EVOH under the EVAL™ trade name in Japan and Asia Pacific and via its subsidiaries Kuraray America, Inc. and EVAL Europe n.v. in the rest of the world.

EVAL™ has been around since 1972 in different applications and it is best known for its oxygen barrier to extend shelf life in food packaging and for its hydrocarbon vapor barrier that allows automotive plastic fuel tanks to meet stringent VOC emission government standards.

... a random copolymer of

Ethylene and **V**inyl **AL**cohol



FUMIGATION (MULCH) FILMS

Fumigation film is a flexible film used to provide both moisture barrier and fumigant vapor barrier in applications where the soil intended for the intensive cultivation of fruits and vegetables undergoes a pre-plant chemical sterilization or fumigation. The fumigation is needed to control soil borne pathogens such as nematodes, as well as bacteria, fungi and weeds.

EVAL™ IN FUMIGATION FILMS

Fumigation films are commonly produced in the thickness range of 0.8 - 1.8 mils and are multilayer in nature. Standard Polyethylene (PE) films are typically either 3-layer clear or 3-layer black/white films that provide good moisture barrier but do not provide a substantial barrier to the typical fumigants used to sterilize the soil. TIF™ or “totally” [mulching] impermeable film is a thin film fabricated by the coextrusion of EVAL™ with Polyethylene and other functional polymers to make a thin, tough, high fumigant vapor barrier coextruded film. TIF films are best produced using 7-layer or higher blown film coextrusion technology. TIF development started in the summer of 2007 with initial permeation and development trials conducted by Kuraray at the University of California, Davis (UC Davis). Since then, numerous successful trials, hundreds of applications and commercial deployments have led to recognition by the U.S. Environmental Protection Agency (USEPA) as a legitimate methyl bromide alternative by incorporating TIF into their Re-registration Decision Eligibility (REDS) fumigant regulations.

TYPES OF FUMIGATION FILMS BY METHOD OF APPLICATION

Row mulch and broadcast film are two main types of applications of fumigation film used in the United States and around the world. Row mulch typically used for drip fumigation and broadcast mulch typically used for shank injection systems Row mulch films are left on the soil for typically a minimum of two crop cycles and the bed may be treated with a pesticide between cycles. In the case of row mulch, films must be stabilized against the detrimental effect of ultraviolet (UV) light on the mechanical properties of the polymers used to produce the film. Broadcast films are left on the soil only for the short period of time needed for the fumigant to perform its sterilization function. This pre-plant period for broadcast films tends to be in the 7 to 21 days. The UV light stabilization package is not normally required for the broadcast film application. EVAL resins can be used in both types of applications.

The fumigant barrier of TIF has been studied extensively by various researchers and certified analytical laboratories. In 2008, Kuraray requested UC Davis to measure the fumigant permeation coefficients for 1.5 mil thick films using 10% core layer of two different grades of EVAL in comparison to other Nylon and PE core layers. The Nylon containing films are known in the industry as VIF or “virtually impermeable films”. The results demonstrated the barrier benefit of TIF directly over other film technologies.

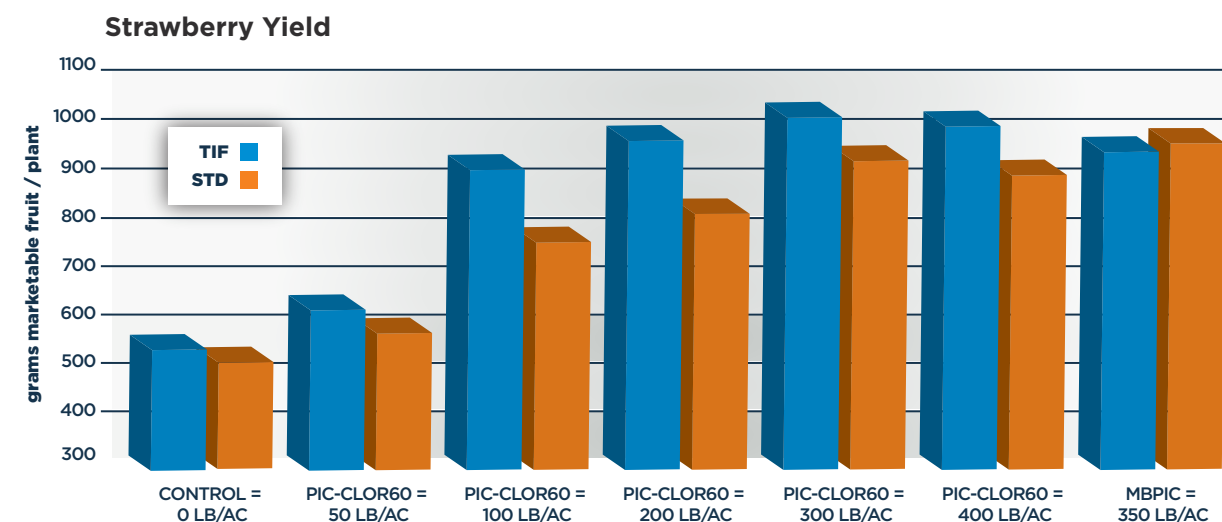
PROPERTIES OF BARRIER MATERIALS IN FLEXIBLE FOOD PACKAGING

Film Type	TIF	VIF	PE	PE
Core Layer Technology	EVAL H171	EVAL SP292	Nylon 6,66	LDPE
Methyl Bromide	0.0001	0.0004	0.47	2.35
Methyl Iodide	0.0001	0.0002	0.33	3.30
Chloropicrin	0.0004	0.0018	1.20	3.84
Cis 1,3-dichloropropene	0.0013	0.0043	1.73	3.93
Trans 1,3-dichloropropene	0.0012	0.0048	0.36	2.98

TIF FILMS MAKE FUMIGANT RATE REDUCTION POSSIBLE

A unique benefit of TIF™ over other mulching films such as VIF and PE films is the fumigant rate reduction potential. This feature provides a win-win situation to all stakeholders involved as there is less environmental impact (EPA), reduced health risks (workers and bystanders), improved farm utilization (grower) and the reduction in fumigant cost can offset the additional cost of the film over lower barrier alternatives.

YIELD OF STRAWBERRY TRIALS CONDUCTED BY UC DAVIS WITH PIC-CLOR60 AND TIF



Additionally, sulfur containing compounds like dimethyl sulfide (DMDS) have been found to be effective fumigants for tomatoes and other crops. DMDS poses a public relation issue to the industry due to the harsh, lingering odor in the surrounding community after it is applied. Virginia Tech has shown in multiple trials the DMDS rate reduction potential with TIF. In a study conducted during the fall of 2010 with tomatoes, it was demonstrated that TIF has a higher DMDS retention rate than medium barrier fumigation film such as VIF. It was also demonstrated that DMDS application rates can be cut from 60 gallons per acre (GPA) with VIF to 30 GPA with TIF without sacrificing productivity or having any type of weed (nutsedge) control issue.

YIELD AND WEED DENSITY OF TOMATO TRIALS BY VIRGINIA TECH WITH DMDS AND TIF

Treatment	Marketable yield (lb/A)	Nutsedge/ft2
Untreated VIF	19735 c	23.8 a
Untreated VIF	32501 b	8.93 b
20 GPA TIF	43772 ab	0.39 c
30 GPA TIF	34727 b	0.13 c
40 GPA TIF	42616 ab	0 c
50 GPA TIF	46331 ab	0 c
60 GPA VIF	45429 ab	0.023 c

REGULATORY DRIVER FOR TIF

Methyl bromide, one of the most effective fumigants used in intensive cultivation of fruits and vegetables, has been declared by the United Nations as an ozone-depleting substance and there is a mandate to phase it out most uses in agriculture by the year 2015. Alternative fumigants such as chloropicrin, 1,3-dichloropropane and methyl iodide although less harmful to the environment are still quite toxic in nature and limiting human exposure is still a critical consideration of the regulating bodies. So for both ecological and health reasons the use of a high barrier mulch film has a positive effect on the continued utilization of fumigation as a means to produce high quality fruits and vegetables in mass scale. After numerous flux, efficacy studies and a better understanding of the performance of mulching films the EPA has proposed the following buffer zone credit guidelines based on fumigant permeation coefficients of the films.

RESULTS OF USEPA CLUSTERING OF FILMS BASED ON FILM TYPE FUMIGANT BARRIER

Film type	Diffusion coefficient, cm/hr	Buffer zone credit relative to PE
PE	2 - 6	—
Metalized films	0.2 - 2.0	20%
VIF	<0.2	40%
TIF	<0.02	60%

In addition to the type of mulch film selected, other mitigation tools can be used by growers to gain USEPA buffer zone credits. For example, taken all mitigation tools into consideration, in the case of chloropicrin, the selection of TIF as the mulch film provides an attractive option for the growers to maximize cultivation area in their farms.

FIGURE 2 OXYGEN BARRIER VS. FLEX CRACK CYCLES

Condition	Reduction in Chloropicrin Buffer Zone
Untreated VIF	20% (metalized), 40% (Nylon based VIF), 60% (EVAL based TIF)
Untreated VIF	10% (OM 1% - 2%), 20% (OM >2% - 3%), 30% (OM > 3%)
20 GPA TIF	10%
30 GPA TIF	10%
40 GPA TIF	15%
50 GPA TIF	15%
60 GPA VIF	80%

Numerous field studies to measure the fumigant emissions (flux studies) have been conducted while being monitored by researchers from UC Davis, the United States Department of Agriculture (USDA), the California Department of Pesticides Regulations (CDPR) and USEPA.

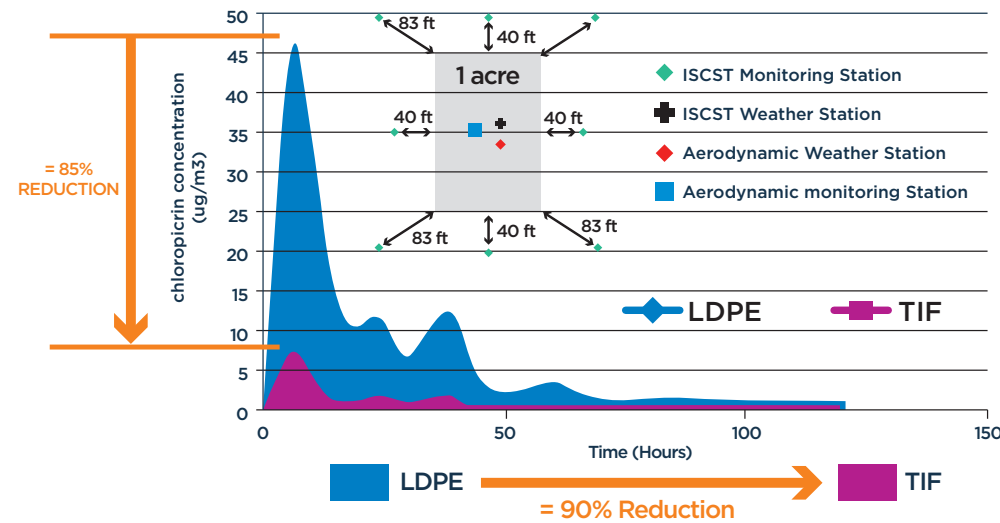


FUMIGANT EMISSION STUDIES

In this particular study done with drip-applied chloropicrin, TIF™ was able to reduce the peak emission by nearly 85% relative to the standard polyethylene mulch. Reduction of peak emissions is of relevance to growers with farms encroaching on residential developments as the data has been correlated by the regulation bodies to the buffer zones (areas of no fumigation) established to reduce human exposure and relevant health risks.

TIF CAN SIGNIFICANTLY REDUCE VOC EMISSIONS

Monitored field trials supervised by Dr. Husein Ajwa of UC Davis have shown TIP reduced drip-applied chloropicrin peak and total emissions by about 85% compared to standard HDPE film.



Drip fumigation testing conducted by the University of California Davis, Plant Sciences Department in Salinas (Two studies: Sep-07 and validation study started in Sep-08)

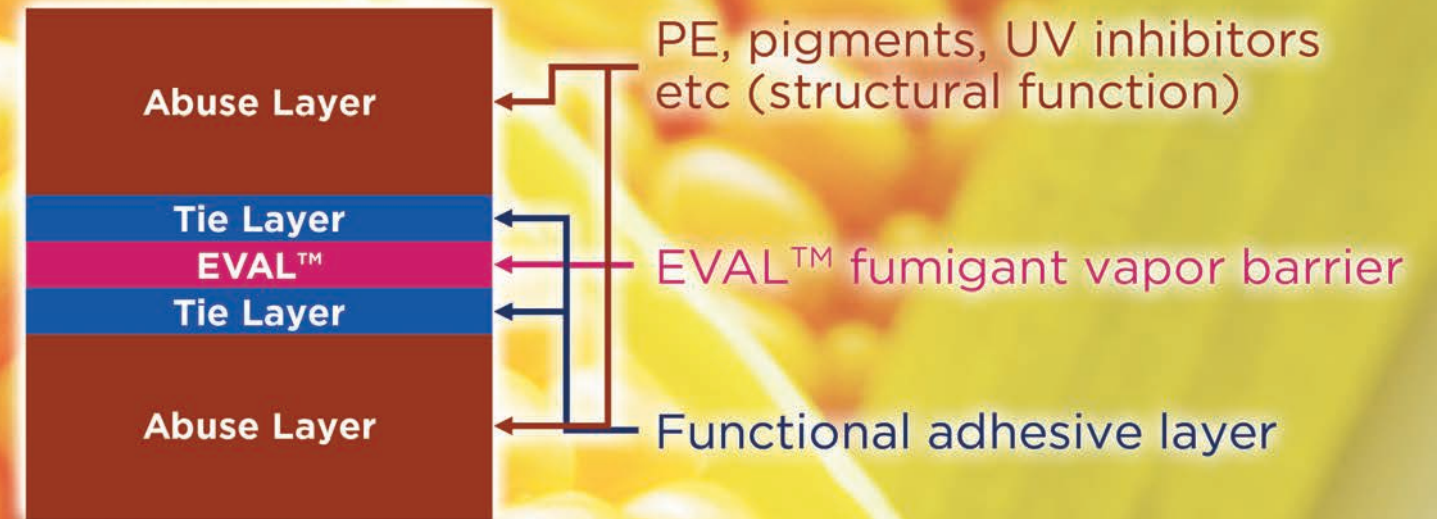
A different flux study conducted with broadcast, shank-applied methyl bromide in California's Wasco County in 2009 - 2010 demonstrated 71 - 90% reduction in peak emission.

Treatment	MB:Pic Applied*	MB Conc**	Emissions Reduction
USEPA RED (tarped broadcast)	360	133.7	—
Untreated VIF	360	119.2	11%
20 GPA TIF	360	38.8	71%
30 GPA TIF	360	23.2	83%
40 GPA TIF	360	26.9	80%
50 GPA TIF	360	178.3	—
60 GPA VIF	180	17.5	90%

* Application rate of MB:Pic = 50/50 in lb/A
 ** Average Methyl Bromide concentration at 24 hours in $\mu\text{g}/\text{m}^2/\text{sec}$

TIF FILMS PROVIDE A ROBUST SOLUTION

A well designed TIF mulching film has mechanical properties which are well suited for field deployment because their core layer is composed of a thin layer of EVAL. The typical commercial structure of a TIF film is 25 - 30 μm with approximately 1.5 μm of EVAL.



The abuse resistance of TIF films has been evaluated in different occasions after field deployment and the fumigant permeation coefficients were confirmed to be $<0.02 \text{ cm/hr}$.

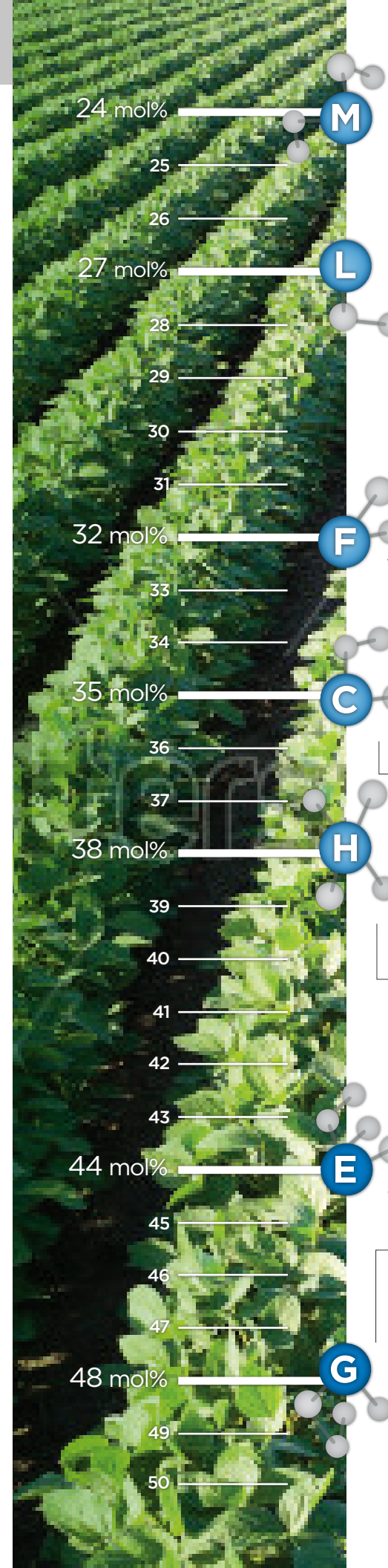
FUMIGANT DIFFUSION COEFFICIENTS BEFORE AND AFTER FIELD DEPLOYMENT MEASURED AT 23°C, 50% RH (CM/HR) BY UC DAVIS

Film	(mils)	Chloropicrin		Cis 1,3-dichloropropene		Trans 1,3-dichloropropene	
		Before	After	Before	After	Before	After
PE	0.95 ± 0.05	2.8	2.8	3.8	3.9	4.3	4.3
TIF	1.00 ± 0.05	0.0001	0.0003	0.0001	0.0027	0.0009	0.0033

EVAL GRADES FOR MULCHING FILMS

Kuraray has several options for the development of TIF film. The preferred grades for the coextrusion of TIF films are our higher ethylene content grades. The grade selection will depend on the capability of the coextrusion equipment and the selection of the complementary polyolefin components that are required for the production of the film.

EVAL™ grade	ρ (g/cc)	Et. (mol%)	M1190 (g/10min)	OTR @ 20°C, 65%RH (cc.mil/100in ² .day)	Tm (°C)
H171	1.17	38	1.7	0.036	172
E171	1.14	44	1.7	0.076	165
SP292	1.13	44	2.0	0.090	161



EVAL™ ethylene vinyl alcohol (EVOH) copolymer resins are characterized by their outstanding gas barrier properties and by their excellent process ability.

The key to this balance of characteristics is the combination of the proper copolymerization ratio of ethylene to vinyl alcohol. Kuraray's unique proprietary manufacturing process has produced the world's widest available range of EVOH grades.

EVAL™ M type offers superior barrier performance for automotive applications.

EVAL™ L type has very low ethylene content and is suitable as an ultra-high barrier grade in several applications.

EVAL™ F type offers superior barrier performance and is widely used for automotive, bottle, film, tube and pipe applications.

EVAL™ C type can be used for high-speed co-extrusion coating and cast flexible applications.

EVAL™ H type has a perfect balance between high barrier properties and long-term run stability and is especially suitable for blown film.

EVAL™ E type has a higher ethylene content which allows for greater flexibility and even easier processing. Different versions have been specially designed for cast and blown film as well as for pipe.

EVAL™ G type has the highest ethylene content, making it the best candidate among standard EVAL™ grades for stretch and shrink film applications.

EVAL™ SP resins are a new family of resins that combine the gas barrier performance of traditional EVOH resins with improved orientability. This "softer" EVOH is ideal for applications where orientation is key and more flexible barrier polymer is needed.



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Rev 9/2012



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