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(54) Title: OLEFIN POLYMER BARRIER FILMS AND METHODS FOR USE THEREFOR		
(57) Abstract <p>Olefin polymer films are produced comprising amounts of one or more permeability reducing fatty acid derivative compounds. The resultant films have improved barrier abilities as evidenced by reduced methyl bromide diffusion rates. The films are very suitably employed as soil fumigation tarpaulins or soil covering materials. Improved methods for confining chemical treatment agents are also taught.</p>		

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OLEFIN POLYMER BARRIER FILMS
AND METHODS FOR USE THEREOF

This invention relates to films made from olefin polymers. It has been found that the addition of certain derivatives of fatty acids to olefin polymer films reduces the permeability of said films. The invention also relates to methods of confining chemical treatment agents to areas of application and adjacent areas desired to be treated. The subject olefin polymer films have been found to be very suitable for confining chemical treatment agents.

Olefin polymer films containing various types of additives are generally known in the art. One problem, however, observed in the films currently known is in achieving desired combinations of resin cost, polymer processability, film strength and film barrier ability. This problem is particularly acute in the area of films used for confinement of chemical treatment agents, and especially soil treatment tarpaulins or soil covering materials. For these and similar uses, large amounts of film are used to confine chemical



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treatment agents to the area where they are applied and are desired and expected to treat. The chemical treatment agents used, which are often very volatile gases, tend to diffuse, wash, dissolve or blow away unless prevented from doing so. The rapid loss or escape of these treating chemicals can be undesirable for several reasons. For example, (1) the chemicals may be hazardous or toxic in some way, (2) the desired treating effects may not be achieved, and/or (3) larger amounts of chemical may be required to achieve the desired effects. The problem of finding a film suitable for use as a chemical treating agent confinement film is further complicated by the fact that during usage such films are subjected to conditions and treated in a manner that punctures and tears in such films tend to occur.

The films currently used to confine chemical treatment agents and as soil treatment tarpaulins or soil covering materials are most commonly low density polyethylene films approximately 25.4 microns (1 mil) thick. Due primarily to their ability to resist puncturing and their ability to resist tear propagation should the film become punctured, these films are fairly well-suited for this usage. The main problem with these films, especially when used with volatile gaseous soil fumigation compounds such as methyl bromide (MeBr) and chloropicrin, is the permeation of the volatile gases through the film and out into the atmosphere. These soil fumigation substances escaping into the atmosphere, depending on their composition, can then present various types of environmental hazards.



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This loss of fumigant due to diffusion, unless prevented by using thicker, more expensive films, requires the application of larger doses of fumigant at a greater expense to ensure that a sufficient amount of the substance remains in the soil to achieve the desired soil treatment effects.

It is also known in the art that fatty acid amides can be added to olefin polymer films in small amounts (i.e., 0.5 percent by weight or less for non-filled films) as slip or anti-block agents making such films easier to handle and use. See, for example, U.S. Patents 3,330,796; 3,645,822; 3,562,291; 2,770,608; 2,938,879 and 3,176,021.

It is an object of the present invention to provide novel olefin polymer films with improved barrier abilities, which films can be easily produced at low cost and are sufficiently resistant to puncturing. It is also an object of this invention to provide a method of confining a chemical treatment agent to areas of application and adjacent areas desired to be treated, which method uses for such confinement purposes olefin polymer films having good barrier abilities along with other desirable physical properties.

According to the present invention there is provided an olefin polymer film comprising a permeability--reducing amount of one or more fatty acid derivative compounds, which film has reduced permeability to the diffusion therethrough of a



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gaseous chemical treatment agent due to the fatty acid derivative compound. In a preferred aspect of the present invention, the fatty acid derivative compound is a fatty acid monoamide such as stearamide.

The present invention also provides a method of confining a gaseous chemical treatment agent to areas of application and adjacent areas desired to be treated, which method utilizes for such confinement purposes olefin polymer barrier films comprising an effective amount of one or more of the above-described fatty acid derivative compounds.

In general, olefin polymer resins suitable for producing films according to the present invention are well known in the art and include polymer resins containing polymerized therein a major amount of ethylene or propylene. As used herein the terms polyethylene and polypropylene refer to polymers having polymerized therein at least 50 percent by weight ethylene or propylene, respectively, preferably at least 70 percent by weight.

Films prepared from the various polyethylene resins are especially preferred in the practice of the present invention. Films made from low density polyethylene (LDPE) can be very advantageously modified according to the present invention to provide desirable barrier films. Films of linear low density polyethylene (LLDPE) (polymers of ethylene and up to about 20 percent by weight of one or more α -olefins having from 3 to 25



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carbon atoms) or blends of LLDPE with high density polyethylene (HDPE) and/or with LDPE provide very desirable barrier films due to superior barrier ability and very good toughness.

It is contemplated within the scope of the present invention to use fatty acid derivative compounds to modify the permeability of olefin polymer resin films. The polymer(s) may include minor amounts of additional, copolymerizable monomers polymerized therein, in addition to the ethylene, the propylene, or in the case of LLDPE, the ethylene and copolymerized α -olefin monomer(s) having from 3 to 25 carbon atoms.

The essence of the present invention lies in the use of one or more permeability reducing derivatives of fatty acids to improve the barrier ability of olefin polymer films and the use of such films to contain gaseous chemical treatment agents. The fatty acids, from which derivatives suitable for the practice of the present invention are prepared, are carboxylic acids generally composed of a chain of from 6 to 24 carbon atoms (including the carboxyl group carbon). The preferred derivatives are monoamides, bisamides, amines and esters of polyhydric alcohols (polyols). The preferred groups of fatty acid derivatives from which permeability reducing compound or compounds can be selected can be represented by the following Formulas I through IV.



I. Monoamides

It has been found that monoamides according to the following formula can improve the barrier ability of olefin polymer films:



wherein R_1 is an alkyl or alkenyl group having from 5 to 23 carbon atoms, preferably from 8 to 20 carbon atoms, R_2 and R_3 are independently a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms, an alkenyl group having from 2 to 24 carbon atoms or an acyl group having from 10 to 24 carbon atoms. Preferably R_2 and R_3 are hydrogen atoms. Monoamides are a particularly preferred group of fatty acid derivatives based on their cost, availability and effectiveness. Exemplary monoamides include stearamide, oleamide, and stearyl stearamide. For a further listing of some of the saturated fatty acid amides represented by this formula see U.S. Patent 4,214,054.

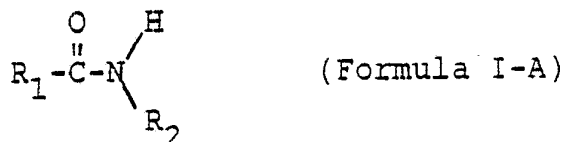
In the above formula and those that follow, it is understood that the various hydrocarbon R-groups can be inertly substituted and that such substitutions do not take the fatty acid derivative compounds outside the scope of the present invention. As used herein the term "inertly substituted" means substitutions or substituent groups comprising atoms other than carbon or hydrogen which substitutions or substituent groups



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do not cause the inertly substituted fatty acid derivative compound to be detrimentally affected by film-producing temperatures and conditions nor do such substitutions or substituent groups otherwise cause the fatty acid derivative compounds to deleteriously effect the olefin polymer film although they might, in fact, improve the barrier or other properties of the film.

One group of monoamides from which the permeability modifying compound(s) can be selected is the group of saturated fatty acid amides which can be represented by the formula:



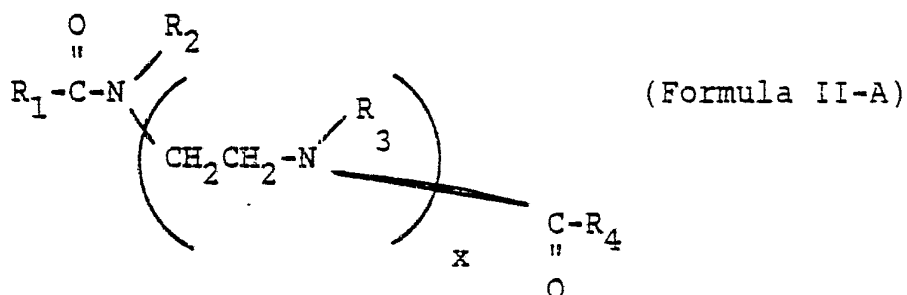
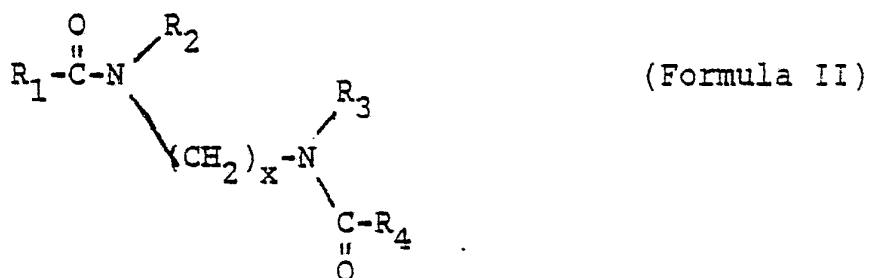
in which formula R_1 is an alkyl group having from 9 to 23 carbon atoms, and R_2 is independently either a hydrogen atom or an alkyl group having from 1 to 24 carbon atoms.

Amides according to the above Formula I-A are exemplified by, but not limited to, stearyl stearamide and stearamide. Saturated amides suitable for the practice of the present invention, such as stearyl stearamide and stearamide, are, in general, commercially available. For example, stearamide sold under the trade name Kemamide® S and stearyl stearamide sold under the trade name Kemamide® S-180, are commercially available from the Humko Chemical Division of Witco Chemical Corporation, Memphis, Tennessee.



II. Bisamides

Bisamides selected from the group of compounds represented by the following Formulas II and II-A can also improve the barrier ability of olefin polymer films.



wherein R₁ and R₄ are independently either an alkyl or alkenyl group having from 5 to 23 carbon atoms, R₂ and R₃ are independently either a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms or an acyl group having from 10 to 24 carbon atoms, and X is an integer from 1 to 6.

Examples of some fatty acid bisamides include N,N'-ethylene bislauramide, N,N'-ethylene bisstearamide and the like.

III. Fatty Acid Amines

According to the present invention fatty acid amines selected from the group of compounds represented by the following formula can be used to improve the barrier ability of olefin polymer films



wherein R_1 is an alkyl or alkenyl group having from 10 to 24 carbon atoms and R_2 and R_3 are independently a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms, or a substituent containing a group of the formula $\{R_4O\}_m$, wherein R_4 is an alkylene group having from 1 to 5 carbon atoms and m is an integer from 1 to 10.

Fatty acid amines suitable for the practice of the present invention are generally known and commercially available. Exemplary fatty acid amines include stearamine and many others. See U.S. Patent 4,214,054 for a further listing of saturated fatty acid amines.

IV. Fatty Acid Esters of Polyols

It has also been found that partial and complete fatty acid esters of polyols (polyhydric alcohols) selected from the group of compounds represented by the following formula can be used to improve the barrier ability of olefin polymer films.



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wherein Z is the residue of a polyhydric alcohol having ℓ hydroxy groups with ℓ being an integer of from 2 to 8, R_1 is independently an acyl group having from 9 to 23 carbon atoms or hydrogen wherein the number of hydrogen R_1 groups is from 0 to $\ell-1$, R_2 is an alkylene group having from 1 to 5 carbon atoms and k is an integer from 0 to 7.

Examples of such compounds include glycerol monostearate and sorbitan monostearate and the like. For a further listing of such fatty acid esters of polyols see U.S. Patents 4,214,054 and U.S. 3,644,230.

Though not intending to limit the scope of the invention, it is theorized that the described compound(s) migrate to the surface of the olefin polymer film to create a thin layer which serves as the barrier to permeating or diffusing gases. Therefore, according to the present invention, enough of the selected compound or compounds which is sufficient to create this layer is added to the olefin polymer, greater amounts not further improving barrier ability noticeably.

It has been found that amounts of the above-described fatty acid derivative compounds up to 5 percent by weight based on the total weight of the olefin polymer plus selected compound(s) continue to improve the barrier ability of such polymer films. It is, however, known in the art to use up to 0.5 percent by weight of some fatty acid monoamide compounds as slip and/or anti-block agents in polyethylene and



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polypropylene films not containing fillers or pigments. It is also known to use up to 1.25 percent by weight of some fatty acid monoamide compounds in polyethylene films (up to 2 percent by weight in polypropylene films) as slip and/or anti-block agents when the films contain filler and/or pigments. Therefore, the presently claimed films involve (a) the use of greater than 0.5 percent by weight fatty acid monoamide in films of polyethylene and polypropylene containing essentially no filler or pigment, (b) the use of greater than 1.25 percent by weight fatty acid monoamide in polyethylene films containing a filler or pigment, (c) the use of greater than 2 percent by weight fatty acid monoamide in polypropylene films containing a filler or pigment and (d) the use of a permeability reducing amount of the other types of fatty acid derivative compounds in polyethylene or polypropylene films with or without a filler and/or pigment. The above and following weight percentages are based on the total weight of (a) olefin polymer, (b) filler/pigment (if any) and (c) fatty acid derivative compound in the olefin polymer films.

It has been found preferable in polyethylene films containing essentially no filler or pigment to use greater than 0.5 percent by weight of fatty acid derivative compound(s), more preferable to use greater than 1 percent by weight and most preferable to use greater than 1.25 percent by weight. In polypropylene films containing essentially no filler or pigment it is desirable to use greater than 0.5 percent by weight of



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fatty acid derivative compound(s), more desirable to use greater than 1 percent by weight and most desirable to use greater than 2 percent by weight.

While olefin polymer films pursuant to the present invention containing more than 5 percent by weight fatty acid derivative compound have reduced permeability to the diffusion of gases such as MeBr, adding amounts greater than 5 percent by weight does not improve the barrier ability of the film substantially. Amounts greater than 5 percent by weight, however, can cause the resin/modifier mixture to be hard to process and to be formed into a film, especially by blown film techniques. Therefore, it is desirable to use amounts of fatty acid derivative compound(s) of 5 percent by weight or less in olefin polymer films and more desirable, especially in the case of polyethylene films, to use 2 percent by weight or less.

For the purpose of claiming the films according to the present invention, the films are viewed as comprising the olefin polymer resin and an additive package. As used herein, "additive" describes (a) the amount and type of fatty acid derivative compound(s) and (b) whether or not the claimed film contains a filler and/or pigment. In general, a film is deemed to contain a filler if there is present in the film more than 10 percent by weight of the filler, and is deemed to contain a pigment if there is present in the film more than 1.0 percent by weight of the pigment



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compound(s). The terms "filler" and "pigment" are well known in the art and include materials such as carbon black, titanium dioxide, calcium carbonate, mica and the like.

It has been found that the fatty acid derivative compound(s) surprisingly reduce the rate of diffusion of gaseous chemical treatment agents such as MeBr through olefin polymer films by more than 10 percent, oftentimes more than 20 percent and in some cases more than 25 percent, compared to the same olefin polymer film not containing any fatty acid derivative compound. The reduction in gaseous chemical treatment agent diffusion, with little or no loss of the physical properties nor increase in film cost allows a reduction in the amount of treatment agent which is required to be applied. This reduction in chemical treatment agent of course results in reduced costs for the overall chemical treatment process as well as other benefits.

The selected compound(s) may be incorporated in the olefin polymer by any of the methods known in the art to be suitable for insuring a uniform mixture of olefin polymer and additive in the final fabricated article. Suitable methods include addition of the compound(s) as a solid, in solution or in the form of a slurry in water or other non-solvent, to the olefin polymer in powder or granule form followed by drying, if necessary, and tumbling. The fatty acid derivative(s) may also be incorporated in the olefin polymer by melt blending the ingredients in a conventional apparatus



such as by being pumped into an extruder which is used to prepare the films, or by other mixing means which includes, e.g., a Banbury Mixer, heated rolls, a plasticator or a fluted liner extruder. A concentrate of the compound(s) in olefin polymer can be made by one of the aforesaid methods and this, in turn, can be blended with olefin polymer by tumbling or other suitable means. Finally, various combinations of the above methods can be used.

The method and apparatus for producing films according to the present invention, and for producing films suitable for chemical treatment agent confinement usage, from olefin polymer resins are well known in the art. See for example, U.S. Patents 3,976,733 and 4,025,253. Also known are the so-called "mesh" films which are particularly advantageous films for the practice of the present invention and methods and apparatus for producing such mesh-type films. In the production of mesh-type films, differential cooling of the extruded film surface causes ribs or areas of greater thickness that reinforce the film allowing overall film thicknesses to be generally reduced. See for example, U.S. Patent 4,315,963.

Films according to the present invention can vary in average thickness depending on their intended usage. The films used for confining chemical treatment agents generally have average thicknesses of up to 254 microns (10 mils). Most soil fumigation tarpaulins generally have average thicknesses of less than 127



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microns (5 mils) and usually from 19 to 38 microns (0.75 to 1.5 mils).

In addition to the above-described additive packages, films according to the present invention may also contain various other additives which are known in the art, such as stabilizers and anti-oxidants; as long as such additives are not detrimental to film performance (i.e., toughness and barrier ability). It is sometimes preferable that the films according to the present invention, when used for mulch film purposes as well as chemical treatment agent confinement, contain only such fillers and pigments that cause the films to be black or dark colored. In this aspect, films containing white-colored pigments or fillers such as titanium dioxide are less preferable but may be useful in controlling soil temperature.

In one aspect, the present invention involves a method of confining a chemical treatment agent to areas of application and adjacent areas desired to be treated, which method utilizes for such confinement purposes olefin polymer film containing one or more of the above-described fatty acid derivative compounds. The olefin polymer film used in this method comprises a permeability-reducing amount of one or more of the above-described compounds, depending on the amount that the inherent barrier ability of the particular olefin polymer needs to be improved to produce a film having the desired amount of barrier ability.



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As used herein, the term "chemical treatment agent" generally means any chemical or substance that can be applied to or in any way contacted with a specific area and/or material or organism located in that area for the purpose of achieving various desired effects. By the terms "confining a chemical treatment agent to its areas of application and adjacent areas desired to be treated" it is meant that chemical treatment agents which are volatile, soluble and/or dust-like in nature and, therefore, may tend to diffuse, dissolve and/or blow away, are intended to be prevented or hindered from leaving said area in such manners. The rapid loss or escape of the treating chemicals can be undesirable because (1) the chemicals may be hazardous or toxic in some way, (2) the desired treating effects may not be achieved, and/or (3) larger amounts of chemical may be required to achieve the desired effects.

The films of concern in the present invention have been found particularly useful as soil treatment tarpaulins. By "soil treatment" it is generally meant the use of various chemical soil treatment agents, applied to the surface of soil or incorporated into the soil at various depths below the surface for the purpose of achieving various desired effects. Due to the barrier ability of the films claimed herein, and the other good physical properties of olefin polymer films, the present invention has been found particularly useful in confining volatile gaseous chemical soil treatment agents or soil fumigants often used to eradicate or reduce soil-contained pathogens such as



bacteria or fungi in order to prepare soil for planting or treat areas for existing diseases or infestations. After these chemicals are injected into or otherwise applied to the soil, the areas so treated are quickly covered by a tarpaulin preventing the escape of the gaseous materials and maintaining a constant effective concentration in the area desired to be treated. Methyl bromide and chloropicrin, for example, are gaseous chemical treatment agents commonly used for these purposes. It is contemplated that other types of gaseous chemical treatment agents are also suitable for use with the films of the present invention.

Another aspect of the present invention involves the use of the above-described olefin polymer films containing fatty acid derivative(s) and the above-described method of confining a gaseous chemical treatment agent to enclose buildings or structures that are being treated with a gaseous fumigant. A further aspect of the present invention contemplates that the film may be useful in situations where the "application of the chemical treatment agent" is a naturally occurring process. In some cases chemical substances may be naturally occurring or created by natural causes in the soil and those substances, due to various beneficial results, are desired to be retained and concentrated in or near the originating area. In such cases, the present barrier film and method of confining a gaseous chemical treatment agent may be advantageously employed to prevent the escape of such substances.



It should also be noted that unlike films not containing fatty acid derivative compound(s), films according to the present invention surprisingly become more resistant to the diffusion therethrough of gaseous chemical treatment agent after undergoing several cycles of heating to about 50°C and cooling to about 30°C. Heating and cooling cycles are typically encountered by fumigation tarps when they are applied outdoors and undergo heating during the day and cooling at night.

Examples

In the following examples the following resins are used to prepare control and/or example films.

<u>Resin</u>	<u>Density g/cc</u>	<u>Melt Index g/10 min.</u>
LDPE 1	0.9245	1.90
LDPE 2	0.9220	1.15
LDPE 3	0.9215	2.00
LDPE 4	0.92	2.3
HDPE	0.965	0.7
LLDPE 1	0.917	2.3
LLDPE 2	0.926	2.0
LLDPE 3	0.930	0.8

Example Films 1-4 - Monoamide Additives in LDPE

Example films 1 through 4 are made using the amide additives and amounts specified in Table I, below. These additives are dry blended with a low



density polyethylene resin LDPE 4. This mixture is then extruded through a 2.54 cm (1 inch) Killion mini-blown film line and film samples 1 through 4 thereby produced. The temperature of the hopper zone into which the mixture is loaded is 21° C (70°F). The barrel temperature ranges from 93 to 177°C (200 to 350°F) with the die being at 177°C (350°F). The die circumference is 5.1 cm (2 inches), the die gap is 0.09 cm (0.035 inch), and the blow up ratio is 2 to 2.5, producing a film 25.4 microns (1 mil) thick. Table I below summarizes the additives and the amounts of such additives employed in the production of example films 1 through 4.

The tables below also summarize the rates at which methyl bromide diffuses through samples of each of the example films. The methyl bromide diffusion rates for the example films are determined by a method which approximates soil treatment conditions. The method is described in an article by M. J. Kolbezen and F. J. Abu-El-Haj published in the "Proceedings of the International Agricultural Plastics Congress 1977" at pages 476 to 481.

In this method, a 10 cm by 40 cm sample of the film to be tested, is used to divide a small chamber in half. The two separate chamber portions, both at approximately atmospheric pressure, therefore, share the film as a common wall, one chamber simulating the atmosphere between the soil treatment tarpaulin and the soil (known as the "soil side" chamber), the other



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chamber representing atmospheric conditions above the soil treatment tarpaulin. Into and through the "soil side" chamber is passed a continuous stream of air containing a constant known concentration of methyl bromide. Into and through the other chamber is passed a continuous stream of air containing no methyl bromide, which stream then picks up the methyl bromide that diffuses through the film sample. The amount of diffused methyl bromide is then measured by gas chromatography and the rate of diffusion for the particular film determined or the permeability of the specific resin/modifier combination (independent of film thickness) determined. The diffusion rate is given in milliliters of methyl bromide per hour per square meter of film per milliliter of methyl bromide per liter of air in the atmosphere under the film ($\text{ml/hr/m}^2/(\text{ml/l})$) at 50°C and standard atmospheric pressure. The permeability is given in milliliters of methyl bromide per hour per square meter of film per mil of film thickness per milliliter of methyl bromide per liter of air in the atmosphere under the film ($\text{ml/hr/m}^2/\text{mil}/(\text{ml/l})$) at 50°C and standard atmospheric pressure. The whole apparatus can be maintained at various different temperatures to observe the effect of temperature on the barrier ability of the film.

The average methyl bromide diffusion rate for film having a particular polymer/modifier composition is determined on the basis of tests run on 2 or 3 samples of that particular film. The diffusion rate for each sample is determined at 30°C , the temperature



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raised to 50°C and the rate determined, the temperature lowered to 30° and the rate determined and so on for 2 or 3 heating/cooling cycles for each sample. The average methyl bromide diffusion rate for each composition for each temperature (30° or 50°) is then calculated based on all the diffusion rates at that temperature for all of the samples of that particular composition.

The temperatures (30°C and 50°C) and the cyclic heating and cooling are used to approximate actual soil treatment tarpaulin usage conditions. It should be noted that the barrier ability of the modified films is observed to improve after each of the heating/cooling cycles.



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TABLE I

MONOAMIDE-MODIFIED BARRIER FILMS

	Example Film No.				
	<u>Control 1*</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Amide Additive</u>					
Amount ¹	0	1 pph	2 pph	1 pph	2 pph
Type	--	Stear- amide ²	Stear- amide ²	Stearyl Stear- amide ³	Stearyl Stear- amide ³
<u>Average Methyl Bromide Diffusion Rate in ml MeBr/hr/m²/(ml/l)</u>					
at 30°C	10.8	4.0	3.0	9.4	7.2
at 50°C	22.2	8.3	6.0	19.3	16.2
<u>% Reduction in MeBr Diffusion⁴</u>					
at 30°C	--	62.8%	72.5%	12.7%	33.1%
at 50°C	--	62.7%	73.0%	12.9%	27.0%

* Unmodified low density polyethylene, not an example of the present invention.

¹ Amount of amide additive in film composition in parts amide per 100 parts olefin polymer resin.

² Kemamide® S brand stearamide.

³ Kemamide® S-180 brand stearyl stearamide.

⁴ % Reduction = $\frac{x-y}{x} \times 100$ where x is the diffusion of unmodified PE and y is the diffusion of modified PE



Example Films 5-8 - Monoamide Additives in
Polyethylene Blend Films

Tables II and III below summarize the benefits obtainable in using stearamide to modify films made from blends of various olefin polymers.

The ingredients specified below are used to produce 25.4 micron (1 mil) films with a conventional single-layer, blown film apparatus. Control Film 2 is a polyethylene film made from a blend of 60 percent by weight LDPE 1 polyethylene resin and 40 percent LLDPE 1. In Examples 5 and 6, a mixture of Kemamide S@ brand stearamide (25 percent) and LDPE 3 (75 percent) is added in place of some of the LDPE 1 to produce an amide-modified film having a resin composition similar to that of Control Film 2, with stearamide concentrations of 1 and 2 percent, respectively, based on weight of the blend composition. The tear strengths of Control Film 2, about 160 gm/mil in the machine direction and 440 gm/mil in the transverse direction, remain about the same in Example Films 5 and 6 after addition of the stearamide. Table II below shows the improvement in barrier ability due to the stearamide.



TABLE II

Monoamide-Modified Barrier Films

<u>Film Composition</u>	<u>Control 2*</u>	<u>Example Film No.</u>	
		<u>5</u>	<u>6</u>
Olefin Polymer ¹	60% LDPE 1 40% LLDPE 1	59% LDPE 1&3 40% LLDPE 1	58% LDPE 1&3 40% LLDPE 1
Stearamide Additive ²	None	1%	2%
Average Methyl Bromide Permeability in <u>ml/hr/m²/mil/(ml/l)</u>			
at 30°C	17.2	4.9	3.3
at 50°C	26.2	7.6	6.1
<u>% Reduction in MeBr Permeability³</u>			
at 30°C	--	71.5%	80.8%
at 50°C	--	71.0%	76.7%

* Unmodified olefin polymer film, not an example of the present invention.

¹ Weight percent olefin polymer in film composition based on total weight olefin polymer resins and stearamide modifier.

² Weight percent Kemamide S@ brand stearamide in film composition based on total weight olefin polymer resins and stearamide modifier.

³ % Reduction = $\frac{x-y}{x} \times 100$ where x is the permeability of unmodified PE and y is the permeability of modified PE



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Control Film 3 is a blend of the following amounts of the indicated resins: 10 percent HDPE; 10 percent LDPE 2, 40 percent LLDPE 3, and 40 percent LLDPE 2. Table III, below, shows the improvement in barrier ability when the above-described Kemamide S® mixture is used in place of some of the LDPE 2 to make Examples 7 and 8. The tear strengths of control Film 3, 60 gm/mil in the machine direction and 716 gm/mil in the transverse direction remain about the same after the addition of the stearamide.



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TABLE III

Film Composition	Control 3	Example Film No.	
		<u>7</u>	<u>8</u>
Olefin Polymer ¹	10% HDPE 10% LDPE 2 80% LLDPE 2&3	10% HDPE 9% LDPE 2&3 80% LLDPE 2&3	10% HDPE 8% LDPE 2&3 80% LLDPE 2&3
Stearamide Additive ²	None	1%	2%
Average Methyl Bromide Permeability in <u>ml/hr/m²/mil/(ml/l)</u>			
at 30°C	6.5	6.1	4.3
at 50°C	11.4	11.2	8.4
<u>% Reduction in MeBr Permeability³</u>			
at 30°C	--	6.2%	33.8%
at 50°C	--	1.8%	26.3%

* Unmodified olefin polymer film, not an example of the present invention.

¹ Weight percent olefin polymer in film composition based on total weight olefin polymer resins and stearamide modifier.

² Weight percent Kemamide S@ brand stearamide in film composition based on total weight olefin polymer resins and stearamide modifier.

³ % Reduction = $\frac{x-y}{x} \times 100$ where x is the permeability of unmodified PE and y is the permeability of modified PE



From Tables I through III above, it is clearly observable that the stearamide and stearyl stearamide improve the barrier ability of olefin polymers at 30 and 50°C. In the practice of the present invention, the additives can be advantageously combined with olefin polymer resins having desirable combinations of cost, processability, and toughness to produce very desirable barrier films. Such films are especially suited for use as soil fumigation tarps or soil covering materials.

Examples Films 9-12 - Other Fatty Acid Derivative Additives

Example films 9-12 and Control 4 are made from LDPE 4 and contain the fatty acid derivative additives and amounts specified in Table IV below. These films are prepared by a process similar to that used to prepare Example films 1-8 and Controls 1-3 and evaluated in the same manner. As is shown in Table IV below, the specified fatty acid derivative additives also improve the barrier ability of the olefin polymer films to methyl bromide diffusion.

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TABLE IV

Additional Fatty Acid Derivative Additives

	Control 4*	Example Film Number			
		9	10	11	12
Film Gauge	1.05	0.89	0.89	1.02	0.93
Additive (type)	--	Glycerol mono- stear- ate ²	Sorbitan mono- stear- ate ³	Stear- amine ⁴	N,N'- ethy- lene- bis- laur- amide
		(partial ester)	(partial ester)	(amine)	(bis- amide)
Amount ¹	0	2 pph	2 pph	2 pph	2 pph
Average Methyl Bromide Permeability in <u>mlMeBr/hr/m²/mil/(ml/l)</u>					
at 30°C	15.2	7.0	6.9	7.8	6.4
at 50°C	21.8	22.4	16.3	19.8	12.8
<u>% Reduction in MeBr Permeability⁶</u>					
at 30°C	--	53.9%	54.6%	48.7%	57.9%
at 50°C	--	2.8%	25.2%	9.2%	41.3%

* Not an example of the present invention.

¹ Amount of additive in film composition in parts additive per 100 parts olefin polymer resin.

² Aldo® MSD brand glycerol monostearate commercially available from Glyco Chemicals.

³ Span® 60 brand sorbitan monostearate commercially available from ICI Americas.

⁴ Kemamide® 990 brand stearamine commercially available from Humko Chemical.

⁵ Kemamide® W-50 brand N,N'-ethylene bislauramide commercially available from Humko Chemical.

⁶ % Reduction = $\frac{x-y}{x} \times 100$ where x is the permeability of unmodified PE and y is the permeability of modified PE.



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As can be seen in Table IV above, the addition of the specified compounds improves the barrier ability of the olefin polymer film to the diffusion of MeBr therethrough. This makes such films particularly desirable for use in applications where gaseous fumigants such as MeBr are desired to be retained in an area which is desired to be treated.

As is apparent from the foregoing specification, the present invention is susceptible to being embodied with various alterations and modifications which may differ particularly from those that have been described in the preceding specification and description. For this reason, it is to be fully understood that all of the foregoing is intended to be merely illustrative and is not to be construed or interpreted or restrictive or otherwise limiting of the present invention excepting as it is set forth and defined in the hereto-appended claims.



1. A film having reduced permeability to the diffusion therethrough of a gaseous chemical treatment agent, the film comprising polyethylene and an additive selected from the following groups:

(a) one or more fatty acid monoamide compounds in an amount greater than 0.5 weight percent based on the total weight of polyethylene and monoamide, and containing essentially no pigment or filler;

(b) one or more fatty acid monoamide compounds in an amount greater than 1.25 weight percent based on the total weight of polyethylene, filler, pigment and monoamide, and containing a pigment and/or filler;

(c) one or more fatty acid derivative compounds in an amount greater than 0.5 and up to 5 percent by weight, said compounds being selected from:

- (i) fatty acid bisamides,
- (ii) fatty acid amines, or
- (iii) fatty acid esters of polyols



and optionally includes a filler and/or pigment;

- (d) a combination of (a) and (c); and
- (e) a combination of (b) and (c).

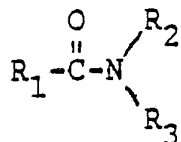
2. The film according to Claim 1 wherein the additive of group (a) is present in an amount greater than 0.5 up to 5 weight percent.

3. The film according to Claim 1 wherein the additive of group (a) is present in an amount greater than 0.5 up to 2 weight percent.

4. The film according to Claim 1 wherein the additive of group (b) is present in an amount greater than 1.25 up to 5 weight percent.

5. The film according to Claim 1 wherein the additive of group (b) is present in an amount greater than 1.25 up to 2 weight percent.

6. The film according to Claim 1 wherein the fatty acid monoamide compound or compounds are selected from the group of fatty acid monoamide compounds represented by the formula:



(Formula I)

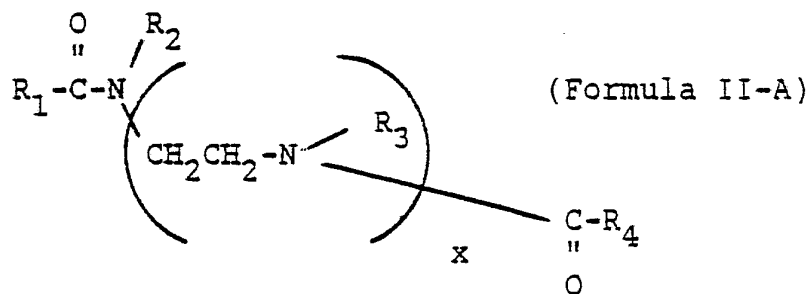
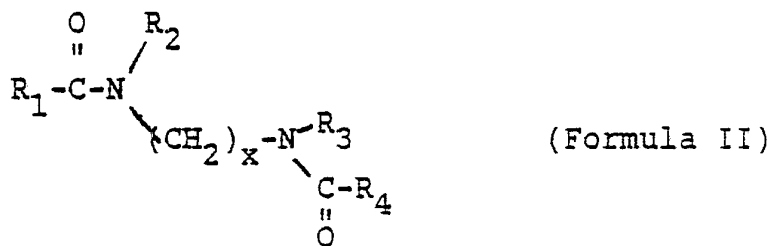


wherein R₁ is an alkyl or alkenyl group having from 5 to 23 carbon atoms, R₂ and R₃ are independently a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms, an alkenyl group having from 2 to 24 carbon atoms, or an acyl group having from 10 to 24 carbon atoms.

7. The film according to Claim 6 wherein the fatty acid monoamide is selected from the stearamide or oleamide.

8. The film according to Claim 1 wherein the additive of group (c) is present in an amount of from 1 to 2 percent by weight.

9. The film according to Claim 1 wherein the fatty acid bisamide compound or compounds of group (c) are represented by the formulas:



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wherein R_1 and R_4 are independently either an alkyl or alkenyl group having from 5 to 23 carbon atoms, R_2 and R_3 are independently either a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms, or an acyl group having from 10 to 24 carbon atoms and X is an integer from 1 to 6.

10. The film according to Claim 1 wherein the fatty acid amine compounds of group (c) are represented by the formula:



wherein R_1 is an alkyl or alkenyl group having from 10 to 24 carbon atoms and R_2 and R_3 are independently a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms, or a substituent containing a group of the formula $\langle R_4O \rangle_m$, wherein R_4 is an alkylene group having from 1 to 5 carbon atoms and m is an integer from 1 to 10.

11. The film according to Claim 1 wherein the fatty acid ester of a polyhydric alcohol compound or compounds of group (c) are represented by the formula:



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wherein Z is the residue of a polyhydric alcohol having ℓ hydroxyl groups with ℓ being an integer of from 2 to 8, R_1 is independently an acyl group having from 9 to 23 carbon atoms, or hydrogen wherein the number of hydrogen R_1 groups is from 0 to $\ell-1$, R_2 is an alkylene group having from 1 to 5 carbon atoms, and k is an integer from 0 to 7.

12. The film according to Claim 1 wherein the diffusion of methyl bromide through the film is reduced by more than 10 percent compared to the same film not containing any fatty acid derivative compound or compounds.

13. A polyolefin film having reduced permeability to the diffusion therethrough of a gaseous chemical treatment agent, the film comprising polyolefin and an additive selected from the following groups:

(a) one or more fatty acid monoamide compounds in an amount greater than 0.5 weight percent based on the total weight of polyolefin and monoamide and containing essentially no pigment or filler;

(b) one or more fatty acid monoamide compounds in an amount greater than 2 weight percent based on the total weight of polyolefin, filler, pigment and monoamide and containing a filler and/or pigment;

(c) one or more fatty acid derivative compounds in an amount greater than 0.5 up to 5 percent by weight, said compounds being selected from:



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- (i) fatty acid bisamides,
- (ii) fatty acid amines, or
- (iii) fatty acid esters of polyols
and optionally includes a filler
and/or pigment;
- (d) a combination of (a) and (c);
- (e) a combination of (b) and (c).

14. The film according to Claim 13 wherein the additive of group (a) is present in an amount greater than 2 weight percent.

15. The film according to Claim 14 wherein the fatty acid monoamide compound is selected from stearamide or oleamide.

16. The film according to Claim 13 wherein the additive of group (b) is present in amount up to 5 percent by weight.

17. The film according to Claim 13 wherein the additive of group (c) is present in an amount greater than 0.5 up to 2.0 percent by weight.

18. The film according to Claim 13 wherein the diffusion of the chemical treatment agent through the film is reduced by at least 10 percent compared to the same film not containing any fatty acid derivative compound.



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19. The film according Claim 1 or 13 having a mesh-type structure.

20. Use of a film according to Claim 1 or 13 for confining a chemical treatment agent to areas of application and adjacent areas desired to be treated.

21. A method of confining a chemical treatment agent to areas of application and adjacent areas desired to be treated, which method utilizes for such purposes an olefin polymer film containing a fatty acid derivative compound in an amount sufficient to reduce the permeability of the film to the diffusion therethrough of a gaseous chemical treatment agent.

22. The method according to Claim 21 wherein said fatty acid derivative compound is present in said film in an amount greater than 0.5 up to 5 percent by weight.

23. The method according to Claim 21 wherein said fatty acid derivative compound is present in an amount of from 1 to 2 percent by weight.

24. The method according to Claim 21 wherein a gaseous chemical treatment agent is used.

25. The method according to Claim 23 wherein the gaseous chemical treatment agent is applied to soil areas.



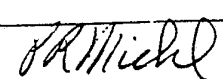
-37-

26. The method according to Claim 25 wherein the gaseous chemical treatment agent comprises methyl bromide.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/01106

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC 9 C08J 9/ 14		
523/132	524/232	
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	523/132 524/230, 232, 306	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 2,938,879, PUBLISHED 31 MAY 1980 MOCK	1-26
X	US, A, 3,176,021, PUBLISHED 30 MARCH 1965 VOLUNGIS ET AL	1-26
X	US, A, 3,562,291, PUBLISHED 9 FEBRUARY 1971 LUTZMANN ET AL	1-26
X	US, A, 3,645,822, PUBLISHED 29 FEB. 1972 WIDIGER	1-26
X	US, A, 3,828,471, PUBLISHED 13 AUGUST 1974 ANDERSON	1-26
X	US, A, 3,875,069, PUBLISHED 1 APRIL 1975 WORSCHER ET AL	1-26
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
SEPTEMBER 6, 1983	13 SEP 1983	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 P. S. KULKOSKY	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	US, A, 3,975,326, PUBLISHED 17 AUGUST 1976 DE VRIEZE	1-26
X	US, A, 4,214,054, PUBLISHED 22 JULY 1980 WATANABE ET AL	1-26
X	JP, B, 43-13372, PUBLISHED 6 JUNE 1968 SUMITOMO CHEM.	1-26
X	DE, B, 2,345,006, PUBLISHED 14 MARCH 1974 DU PONT	1-26

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. Claim numbers, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the International application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

The additional search fees were accompanied by applicant's protest.

No protest accompanied the payment of additional search fees.