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[54]	THERMOPLASTIC MULTI-LAYER
	PACKAGING FILM AND BAGS MADE
	THEREFROM

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		428/520; 426/127
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[56] References Cited

U.S. PATENT DOCUMENTS

428/349, 516, 518, 476.9, 476.3, 520

3,456,044	7/1969	Pahlke .
3,808,304	4/1974	Schirmer.
4,011,382	3/1977	Levine et al
4,064,296	12/1977	Bornstein et al 428/516 X
4,076,698	2/1978	Anderson et al
4,161,562	7/1979	Yoshikawa et al
4,196,240	4/1980	Lustig et al
4,207,363	6/1980	Lustig et al
4,239,826	12/1980	Knott, II et al 428/516 X
4,254,169	3/1981	Schroeder.
4,281,045	7/1981	Sumi et al
4,302,565	11/1981	Goeke et al
4,330,639	5/1982	Matsuura et al
4,335,224	6/1982	Matsuura et al
4,339,181	8/1983	Yoshimura et al
4,399,181	8/1983	Yoshimura et al
4,424,243	1/1984	Nishimoto et al
4,429,079	1/1984	Shibata et al
4,438,238	3/1984	Fukushima et al
4,447,480	5/1984	Lustig et al
4,456,646	6/1984	Nishimoto et al
4,457,960	7/1984	Newsome .
4,469,742		Oberle et al
4,469,753		Yoshimura et al
		Beran et al
- •		Yoshimura et al
		Ohya et al
4,640,856		Ferguson et al 428/36
4,755,436		Garland.
4,863,769	9/1989	Lustig et al

4,863,784	9/1989	Lustig	428/218
4,894,107	1/1990	Tse et al	
4,976,898	12/1990	Lustig et al	
4,988,783	1/1991	Beran et al	
5,059,481	10/1991	Lustig et al	

FOREIGN PATENT DOCUMENTS

533613	12/1980	Australia .
553698	10/1984	Australia .
0002606	6/1979	European Pat. Off.
0120503	10/1984	European Pat. Off.
52-135386	11/1977	Japan .
58-82752	5/1983	Japan .
58-102762	6/1983	Japan .
58-37907	8/1983	Japan .
58-208435	12/1983	Japan .
2066274	7/1981	United Kingdom.
1600250	10/1981	United Kingdom.
2097324	11/1982	United Kingdom.

OTHER PUBLICATIONS

Union Carbide, "Presentation for Cryovac," Sep. 1984.

J. P. Machon, "Actual and Potential Development of High Pressure Process for Linear Polyethylene," Polyethylenes 1933–83, The Plastics and Rubber Institute Golden Jubilee Conference, Jun. 8-10, 1983, pp. B2.5.1-B2.5.8.

S. Kurtz, "VLDPE plugs a gap in PE's density spectrum," Plastics Engineering, Sep. 1985, pp. 59-62.

S. Kurtz, "VLDPE: A Breakthrough in Flexible Linear Polyethylene," ANTEC '85, pp. 463–465.

"Sclair® 11P and 11W Polyethylene Resins," Du Pont Company, Oct. 1980.

"Sclair® Linear Polyethylene Film Resins," Du Pont Canada Inc., printed Jan. 1983.

L. Chriswell, "Modern Processes for the Manufacture of Polyethylene and Polypropylene," Chemical Engineering Progress, Apr. 1983, pp. 84–92.

F. Karol, "The polyethylene revolution," Chemtech, Apr. 1983, pp. 222–228.

M. Concha, "Polyethylene, Linear Low-Density," Packaging Engineering, Jan. 1983, pp. 76–78.

(List continued on next page.)

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[57] ABSTRACT

A thermoplastic, multi-layer packaging film is disclosed which comprises at least 5 layers in which one surface layer is a heat sealing layer and one of the internal layers is a barrier layer. The heat sealing surface layer comprises a copolymer of ethylene and an alpha-olefin having 4 to 8 carbon atoms per molecule and said copolymer comprises 90% to 75% ethylene and 10% to 25% alpha-olefin having 4 to 8 carbon molecules and a density of less than 915 kg/m². The heat sealing layer may also comprise a blend of the aformentioned copolymer with an ethylene/vinyl-acetate copolymer or an ethylene/butyl-acrylate copolymer. The film can be oriented to be heat shrinkable and can be formed into bags by heat sealing portions of the sealing surfaces together. The heat seals have superior cold strength and minimize seal failure when the bags are loaded with relatively heavy products.

21 Claims, No Drawings

OTHER PUBLICATIONS

- "Programme for the International Agents Meeting," DSM Polymers International, Mar. 26–30, 1984.
- "TAFMER®", Mitsui Petrochemical Industries, Ltd.
- "Technical Information on TAFMER® A and TAFMER® P Plastics Modifiers," Mitsui Petrochemical Industries, Ltd.
- "Mitsui Petrochemical in Perspective," Mitsui Petrochemical Industries, Ltd., 1984.
- "Polyethylene producers face tough times," European Chemical News, Dec. 16, 1985, pp. 13–14.
- Packaging, Jan. 1985, pp. 57-60.
- "XP-61512.00 Linear Low Density Polyethylene For Cast Film Extrusion," The Dow Chemical Co., copyright 1984. "Technical Information—XU-61502.43 Linear Low Density Polyethylene," The Dow Chemical Company, Jan. 22, 1986.
- "Technical Information—DowlexTM 4000 Linear Low Density Polyethylene," The Dow Chemical Company, Oct. 16, 1985.
- "Technical Information—DowlexTM 4088 Linear Low Density Polyethylene," The Dow Chemical Company, Mar. 14, 1985.
- "Technical Information—XU-61512.01 Linear Low Density Polyethylene For Blown Film Extrusion," The Dow Chemical Company, Dec. 5, 1984.
- "Technical Information—DowlexTM 2088 Linear Low Density Polyethylene For Cast Film Extrusion," The Dow Chemical Company, copyright 1981, May 23, 1984.
- "Introducing 'Very Low Density PE'", Plastics Technology, Sep. 1984, p. 113.

- "New Kind of Polyethylene Combines Flexibility, Toughness, Heat Resistance," Plastics Technology, Oct. 1984, pp. 13 and 15.
- "Can 'VLDPE' outperform EVA, other copolymers?", Modern Plastics International, Oct. 1984, pp. 6, 8.
- "UC researchers smash 0.915 PE density mark", Plastics World, Oct. 1984, p. 8.
- "Ultralow density PEs are tough, flexible, versatile", Plastics World, Oct. 1984, p. 86.
- "Stamylex PE", Dutch State Mining, Feb. 1984.
- "Now it's very-low-density polyethylene", Chemical Week, Sep. 19, 1984, p. 66.
- "Currents", Chemical Engineering, Oct. 15, 1984, p. 42.
- "TAFMER® . . . A new-type elastomer as Plastics Modifying Agent, supplied in pellet form," dated Aug. 1975.
- "TAFMER® 'A'—A New Polyolefin Resin With Excellent Flexibility," dated Jan. 1977.
- "TAFMER® 'P'—A new-type elastomer as Plastics Modifying Agent, supplied in pellet form," dated Aug. 1975.
- "Design Parameters for LLDPE Film Resin Selection", Polymers, Lamination and Coatings Conference, TAPPI, 1984.
- "TAFMER(R)", Mitsui Petrochemical Industries, Ltd., Aug. 1975.
- "Plastiscope", Modern Plastics Encyclopedia.
- "Stamylex Film Grades", DSM Polymers International.
- "Cast Film", DSM.

1

THERMOPLASTIC MULTI-LAYER PACKAGING FILM AND BAGS MADE THEREFROM

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This application is a continuation of application Ser. No. 10 648,480 filed on Jan. 30, 1991, now abandoned, which in turn is a reissue of U.S. Pat. No. 4,801,486.

The invention relates to thermoplastic multi-layer packaging films and bags or pouches made therefrom. In particular this invention relates to films and bags having superior heat shrink and cold seal properties, which give good seal strength even through contamination like grease or blood, and which allow the application of higher shrink temperatures due to their improved seal strength at elevated temperatures.

Shrinkable and heat sealable thermoplastic films are being used in packaging of non-food and food products like meat, cheese, poultry and the like. Many attempts have been made to combine good shrink properties with satisfactory sealability and good seal strength both at room temperature 25 and at higher temperatures but there is still room for improvement.

A laminate film known from U.S. Pat. No. 3,741,253 comprises a core layer of a vinylidene chloride copolymer between a layer of a cross-linked ethylene-vinyl acetate 30 copolymer used as a sealant and an outer layer of ethylene-vinylacetate copolymer which is not cross-linked. The ethylene-vinylacetate copolymer has improved properties over the previously used polyethylene, especially when it has been cross-linked by irradiation.

As disclosed in U.S. Pat. No. 4,064,296 the core layer may also consist of a hydrolized ethylene-vinyl acetate copolymer. It has similar oxygen barrier properties as vinylidene chloride copolymers and often the advantage that it may be irradiated without discoloration.

Certain advantages have been achieved by using an ionomeric resin as sealing layer. They result in a higher seal strength at elevated temperatures thus allowing higher shrink temperatures. However, their cold seal strength is not fully satisfactory. This latter property is important in modern 45 automated bag packaging processes in which the seals are subjected to substantial stress when the bags are opened and loaded with the article to be packed.

More recently low density linear polyethylenes have become commercially available and have also been pro- 50 posed for packaging applications. Actually the so called linear low density polyethylenes are copolymers of ethylene and varying amounts of higher α -olefins with e.g. 5 to 10 carbon atoms per molecule (U.S. Pat. No. 4,076,698) or 3 to 8 carbon atoms per molecule (published European patent 55 application No. 120503). Depending on their density these materials are referred to as linear low density polyethylene (LLDPE) or very low density polyethylene (VLDPE), the separation line being at a density of about 0.910 g/cm³. Some properties of VLDPE have been described in Plastics 60 Technology, September 1984, page 113 and October 1984, page 13 as well as in a company brochure published in February 1984 by DSM in the Netherlands and entitled "Stamilex PE". Their properties are said to be a unique combination between those of standard polyethylene and 65 polyolefmic rubbers. Their sealability and their compatibility with other polymers has been mentioned.

2

It is an object of the present invention to provide a multi-layer laminated packaging film and bags made therefrom which have improved shrink characteristics over the materials used in the past. This means that at a given temperature the shrink in percent (the mean between the shrink in the longitudinal and transversal direction) should be higher and the tolerated maximum shrink temperature should also be higher. The maximum shrink temperature is dependent on the seal strength at elevated temperatures.

It is a further object of this invention to provide a packaging material with improved cold seal strength and thereby a reduced risk of breakages when bags made of the film material are utilized in automated loading processes.

It is yet another object of the present invention to provide a packaging material which gives reliable seals even when contaminated. Especially in the packaging of meat it frequently occurs that the sealing areas are contaminated with grease or blood, both of which tend to impair the sealing between hitherto used sealing layers.

Finally and most importantly it is an object of this invention to provide a material combining the above advantages, i.e. improved shrinkability, increased maximum shrink temperature, good cold seal strength and sealability through contamination.

It has been found that the above-mentioned objects are achieved by the present invention which is directed to a thermoplastic multi-layer packaging film comprising at least an outer polymer layer, an inner heat sealing layer and optionally an oxygen barrier layer between said inner and said outer layer, and which is characterized in that the heat sealing layer comprises a copolymer of ethylene and x to y% by weight, based on the copolymer, of an α -olefin with 4 to 8 carbon atoms, whereby $x=0.5n_C+8$ and $y=1.25n_C+15$ will n_C being the number of carbon atoms in the α -olefin, said copolymer having a density of less than 920 kg/m³.

Preferably the heat sealing layer comprises a copolymer of ethylene and 12 to 20% by weight, based on the copolymer, of an α -olefin with 4 to 8 carbon atoms.

It has surprisingly been found that both the heat shrink properties and the cold seal strength of the laminated packaging film depend on the comonomer content of the ethylene copolymer used as the sealing layer. In order to achieve optimal results the comonomer content must increase when going from the C_4 - α -olefin (butene(1) to the C_8 - α -olefin (octene(1). It is particularly surprising that the films of the present invention exhibit improved shrink properties both in irradiated (cross-linked) and non-irradiated condition and that these properties as well as the seal strength are a function of the comonomer content of the linear low and very low density "polyethylene".

When using a copolymer of ethylene and butene (1) the comonomer content should be between 10 and 20% by weight, based on the copolymer. Such copolymers have a density of less than 915 kg/m³. When employing a copolymer of ethylene and octene (1) the comonomer content should preferably be increased to between 12 and 25% by weight, based on the copolymer. Such copolymers have a density of less than 920 kg/m³.

According to the invention it is also possible to blend the ethylene/α-olefin copolymer with up to 50% by weight, based on the sealing layer composition, of a polymer which is compatible with said ethylene/α-olefin copolymer. Such further polymer may preferably be selected from the group comprising linear low density polyethylene (LLDPE) with a density above 920 kg/m³, linear high density polyethylene (LHDPE), low density polyethylene (LDPE), ethylene vinyl acetate (EVA), acid modified EVA, polypropylene, ethylene/

propylene copolymer, ionomeric polymers and ethylene/alkylacrylate copolymers wherein the alkyl moiety has 1 to 8 C atoms, in particular ethylenemethylacrylate (EMA), ethylene-ethylacrylate (EEA) and ethylene-butylacrylate (EBA).

The ethylene/alkylacrylate copolymer which can be blended with the ethylene/ α -olefin in the heat sealing layer can comprise 3 to 30% by weight of alkylacrylate.

According to one embodiment of the invention the ethylene copolymer forming the sealing layer may be crosslinked by irradiation in order to improve its shrink characteristics and mechanical properties. However, such crosslinking is not necessary since a very satisfactory packaging film is also obtained without irradiation. If polyvinylidene chloride is used as core layer providing an oxygen barrier the irradiation should take place prior to the lamination of the core layer to the sealing layer since PVDC may suffer when exposed to high energy irradiation. The entire multi-layer film may be irradiated if the PVDC core layer is substituted by a core layer of partly hydrolyzed ethylene vinyl-acetate 20 copolymer (EVOH). PVDC and EVOH are the preferred core layers since they show outstanding oxygen barrier properties.

The films are normally oriented in longitudinal and transversal direction to obtain the desired shrink properties. 25 If a tubular film is produced by extrusion the orientation may be effected using the known air bubble method and further stretching the film by pulling. Alternatively, orientation may be achieved by deep drawing of a planar film.

The outer layer of the multi-layer packaging film of the 30 invention may be of the same ethylene copolymer as the sealing layer, i.e. an ethylene/ α -olefin copolymer comprising 10 to 25% by weight, based on the copolymer, of an α -olefin with 4 to 8 carbon atoms, said copolymer having a density of less than 920 kg/m³ ethylene vinyl acetate and 35 polyamides, and ionomeric resins. It may frequently be of advantage if an adhesive layer and/or an adhesion promoting layer is interposed between said other layers.

If bags are made from the film material the film will normally be folded so that the fold forms the bottom of the 40 bag whereafter both sides are sealed so that the side seals close both sides of the bag. Alternatively a bag may be formed from a tubular film in that the bottom of the bag is formed by a transverse seal across the flattened tube and the mouth is formed by severing the tube at a pre-selected 45 distance from said transverse seal. Pouches can be obtained by sealing two film sheets at three edges.

The invention will be further illustrated by reference to the following examples without being limited thereto. The following test methods were used to investigate the properties of the packaging films and to compare them with other materials,

A. VARIABLE PRESSURE HOT BURST TEST (VPHB)

This is a test to determine the seal quality of shrinkable materials at different temperatures. The approach with this test is to immerse total seal areas into hot water and after a predetermined dwell time, the pressure inside the bag is increased at a constant rate of approx. 25.4 mm of water per second until the seal fails.

The mm of water pressure, at the level at which the seal fails, are recorded, and there are minimum specifications expressed in mm for each bag width. The highest is the number, the better is the seal quality at that temperature.

B. PERCENT SHRINK

The percent shrink is measured immersing for a couple of seconds in hot water a specimen and measuring the percent of retraction, both in the longitudinal and transversal direction. The highest is the percent of shrink, the better is the performance of the material in terms of package presentation.

In practice, the maximum achievable percent of shrink is that measured at the temperature at which the material meets the minimum VPHB requirements expressed in mm of water pressure (see point A). To predict the shrink behaviour it is therefore useful to plot in the same diagram the % of shrink and the VPHB as a function of the temperature.

C. COLD SEAL STRENGTH

The cold seal strength represents the seal quality at room temperature and predicts the seal performance when the bag is loaded with a product either manually or by means of automatic loaders, which operate with a pusher, which pushes the product into the bag. The cold seal strength is measured with a modified pusher of a commercial loader, equipped with a system to record the pressure necessary to open the bottom seal. The head of the pusher operates on a 6 cm length of seal and the cold seal strength is expressed in kg/6 cm. The maximum pressure recordable with this systems is 40 kg/6 cm.

The reported results are the average of 10 measurements. The following raw materials were used in the examples:

RAW MATERIALS										
ABBREVIATION	COMPOSITION	MELTING POINT	DENSITY (g/cm ³)							
E/15% B	ethylene-butene copolym., 15% butene	118° C.	0.906							
E/8% B	ethylene-butene copolym., 8% butene	121.5° C.	0.918							
E/6% VA	ethylene-vinylacetate copolym., 6% VA	105° C.	0.926							
E/9% VA	ethylene-vinylacetate cop., 9% VA	96° C.	0.929							
E/14% VA	ethylene-vinylacetate copolym., 14% VA	90° C.	0.932							
E/18% VA	ethylene-vinylacetate cop., 18% VA	91° C.	0.940							
Ionomer (Na)	Ionomeric resin (Na salt)	90–92° C.	0.940							
E/19% O	ethylene-octene copolym., 19% octene	124° C.	0.911							
E/13% O	ethylene-octene copolym., 13% octene	124° C.	0.915							
E/10.5% O	ethylene-octene copolym., 10.5% octene	123° C.	0.920							
Acid modif. EVA	acid modified Ethylene-Vinylacetate	(55° C.)	0.948							
PA	Polyamide (Nylon 6,12 copolymer)	140–147° C.	1.06							
EMA (20% MA)	ethylene-methylacrylate copolym., 20% MA	85–90° C.	0.942							
EBA (7% BA)	ethylene-butylacrylate copolym. 7% BA	98–108° C.	0.923							

-continued

	RAW MATERIALS		
ABBREVIATION	COMPOSITION	MELTING POINT	DENSITY (g/cm ³)
P/4.5% E	propylene-ethylene copolym., 4.5% E	135° C.	0.900

COMPARATIVE EXAMPLES 1 TO 4 AND EXAMPLES 1 TO 3

Multi-layer packaging films of the composition summarized below in table I were prepared in the following manner. The first two layers A and B were coextruded through a conventional tubular extruder to form a tube. After leaving the die the substrate was cooled and flattened. It was 15 then sent through an irradiation vault where it was irradiated by high energy electrons to a dosage of about 4.5 MR. Depending on the characteristics desired this dosage could vary from 2 to 20 MR. After leaving the irradiation vault the substrate was again inflated and sent through a first tubular 20 extrusion coating die where it received a coating of vinylidene chloride copolymer. Thereafter the still inflated and now triple-walled film passed through a second tubular extrusion coating die where it received a layer of ethylenevinyl acetate copolymer. After the final coating the film was 25 cooled, collapsed and rolled-up. This tape was subsequently unrolled, fed through a bath of hot water, held at a tempera-

ture of about 80° to 98° C., and as it left the water it was inflated and blown into thin tubing with a total wall thickness of about 59 microns. This so-called "trapped bubble" technique is well known in the art. The film was then rapidly cooled to set the orientation and then rolled up for further processing.

The polyvinylidene chloride and the ethylene-vinylacetate copolymer can alternatively be coated onto the substrate using a two-ply coextrusion die.

Thee test results are summarized in the following table II.

TABLE I

	Α	B		D	- 	F		
Exampe No.	sealing layer	μm	core layer	μm	barrier layer	μm	outer layer	μm
Comp. 1	E/9% VA	37			PVDC	В	E/9% VA	14
Comp. 2	Ionomer (Na)	15	E/9% VA	22	PVDC	8	E/9% VA	14
Comp. 3	E/8% B	15	E/9% VA	22	PVDC	8	E/9% VA	14
Comp. 4	E/10.5% O	15	E/9% VA	22	PVDC	8	E/9% VA	14
1	E/15% B	15	E/9% VA	22	PVDC	8	E/9% VA	14
2	E/13% O	15	E/9% VA	22	PVDC	8	E/9% VA	14
3	E/19% O	15	E/9% VA	22	PVDC	8	E/9% VA	14

TABLE II

		<u>.</u>		Exa	mple			
	Comparison 1		Comparison 2		Comparison 3		Comparison 4	
Temperatures	VPHB mm H ₂ O	Shrink % L+T 2	VPHB mm H ₂ O	Shrink % L+T 2	VPHB mm H ₂ O	Shrink % L + T 2	VPHB mm H ₂ O	Shrink % L+T 2
60° C.				4		2		2
70° C.				11		6		7
80° C.	663	21	856	25	855	12	930	14
85° C.	652	30	782		795		841	
90° C.	520	41	608	45	644	24	695	28
95° C.	318	57	438		540		552	
100° C.			268	63	420	42	432	49
COLD SEAL	24,5		15,8		16,1		17,3	
STRENGTH	(10)	Of						
(kg/6 cm)	•	% no. kage)						

		Exa	mple		
Exar	nple 1	Exar	nple 2	Exar	nple 3
VPHB	Shrink %	VPHB	Shrink %	VPHB	Shrink %

TABLE II-continued

Temperatures	mm H ₂ O	$\frac{L+T}{2}$	mm H ₂ O	$\frac{L+T}{2}$	mm H ₂ O	$\frac{L+T}{2}$
60° C.		3		2		4
70° C.		10		7		9
80° C.	1040	27	1051	16	1074	25
85° C.	940		928		990	
90° C.	783	48	745	33	802	49
95° C.	647		558		621	
100° C.	398	64	429	53	363	67
COLD SEAL STRENGTH (kg/6 cm)		22,5		9,4	2	23,5

When comparing the results it should be borne in mind that the shrink temperature should not exceed a value at which the hot-burst pressure drops below 650 mm/H₂O. For some food products the maximum shrink temperature may be more limited but a higher hot-burst will then give additional safety. It is clear from the data in table II that comparison 1 gives good cold seal strength but the hot seal strength and the percent shrink leave something to be desired. Further, this material results in poor seal strength through contamination like gease or blood. Comparision 2 shows improved shrink characteristics but the cold seal strength is considerably lower and this material cannot be sealed reliably through blood contamination.

Examples 1, 2 and 3 show that excellent shrink characteristics and a very good seal strength both at room temperature and at elevated temperatures are being obtained. It has further been found that the seal strength is not significantly affected by contamination like grease or blood. Comparisons 3 and 4 show that a very significant decrease both in seal strength and percent shrink occur when the comono-

mer content in the ethylene α -olefin copolymer drops below a certain level, i.e. the minimum comonomer content is an essential feature if the combination of desired properties is to be achieved.

COMPARATIVE EXAMPLES 5 AND 6, EXAMPLES 4 TO 10

Multi-layer packaging films of the composition summarized in the following table III were produced by conventional techniques, i.e. by coextruding a tubular film of layers A to F and subsequent stretching and orientation, e.g. in the blown-up bubble, so as to obtain a heat shrinkable film. No irradiation was employed in this case. The test results obtained are tabulated in the following table IV.

TABLE III

					<u>C</u>		D)	E			F
Example	<u>A</u>		В		adhesion		barrier		adhesion		outer	
No.	sealing layer	μm	core layer	μm	promotor	μm	layer	μm	promotor	μm	layer	μm
Comp. 5	Ionamer (Na)	25	E/18% VA	9 +	acid modif.	6	PVDC	8	acid modif.	6	PA	23
			E/14% VA	43	EVA				EVA			
Comp. 6	E/8% B	25	E/18% VA	9 +	acid modif.	6	PVDC	8	acid modif.	6	PA	23
			E/14% VA	43	EVA				EVA			
4	E/15% B	25	E/18% VA	9 +	acid modif.	6	PVDC	8	acid modif.	6	PA	23
			E/14% VA	43	EVA				EVA			
5	E/13% O	25	E/18% VA	9 +	acid modif.	6	PVDC	8	acid modif.	6	PA	23
			E/14% VA	43	EVA				EVA			
6	E/19% O	25	E/18% V A	9 +	acid modif.	6	PVDC	8	acid modif.	6	PA	23
			E/14% VA	-43	EVA				EVA			
7	75% E/13% O +	25	E/18% VA	9 +	acid modif.	6	PVDC	8	acid modif.	6	PA	23
	25% EBA		E/14% VA	43	EVA				EVA			
8	90% E/13% O +	25	E/18% VA	9 +	acid modif.	6	PVDC	8	acid modif.	6	PA	23
	10% acid modif.		E/14% VA	43	EVA				EVA			
	EVA											
9	50% E/13% O +	25	E/18% VA	9 +	acid modif.	6	PVDC	8	acid modif.	6	PA	23
	50% E/8% VA		E/14% VA		EVA	_	— ~	-	EVA	-	-	
10	50% F/15% B +	25	E/18% VA		acid modif.	6	PVDC	8	acid modif.	6	PA	23
	50% P/4.5% E	_	E/14% VA		EVA	•	- · - -		EVA	•		

TABLE IV

	Example										
Temperatures	Comparison 5		Comparison 6		Example 4		Example 5		Example 6		
	VPHB mm H ₂ O	Shrink $\%$ $\frac{L+T}{2}$	VPHB mm H ₂ O	Shrink $\frac{L+T}{2}$	VPHB mm H ₂ O	Shrink $\%$ $\frac{L+T}{2}$	VPHB mm H ₂ O	Shrink $\frac{L+T}{2}$	VPHB mm H ₂ O	Shrink % L + T 2	
60° C. 70° C. 80° C.	993	15 25 37	951	4,5 9,5 15,6	1084	13,5 21.5 33,5	1043	5 11 19	1007	9 19,5 33	
85° C. 90° C. 95° C.	877 617 381	43	857	30,6	835	45,0	892 710 534	36	753 560 431	43	
100° C. COLD SEAL STRENGTH (kg/6 cm)	319 46 17,6		599 42,0 25,6		546 55,0 32,7 (70% no. breakage)		436 51 29,6		338 51 28		
			Example								
			Example 7		Example 8		Example 9		Example 10		
	Ten	Temperatures		L+T 2	Shrink % VPHB mm H ₂ O	<u>L+T</u>	Shrink % VPHB mm H ₂ O	$\frac{L+T}{2}$	Shrink % VPHB mm H ₂ O	<u>L+T</u>	
	7	50° C. 70° C. 30° C.	1020	5 12 18	980	6 13 20	940	10 16 20	1150	4 10 18	
	5	35° C. 90° C. 95° C.	850 700 525	35	780 670 510	35	720 610 470	34	810 700 560	34	
	COI STE	100° C. COLD SEAL STRENGTH (kg/6 cm)		410 52 32,0		430 48		320 52		490 44 25	

The results are essentially similar to those obtained with 35 the irradiated material. Only the films of the present invention combine excellent shrink characteristics with outstanding cold and hot seal strength. In addition thereto they may be sealed without impairing the seal strength through contamination like grease or blood which are always encountered in the packaging of meat products. Further, the non-irradiated structures show the same effect, namely a strong dependency of the shrink and seal characteristics on the comonomer content of the ethylene/α-olefin copolymer.

The embodiments of the invention in which an exclusive 45 property or privilege is claimed are defined as follows:

- 1. A multi-layer thermoplastic packaging film having improved heat shrink and cold seal properties, said film comprising:
 - (a) a first surface layer which is a heat sealing surface, said layer comprising:
 - (1) a copolymer of ethylene and an alpha-olefin having 4 to 8 carbon atoms per molecule; and,
 - (2) said copolymer comprising 90% to 75% ethylene and 10% to 25% alpha-olefin having 4 to 8 carbon ⁵⁵ molecules and a density of less than 915 kg/m³;
 - (b) a second surface layer, said layer comprising a polymer selected from the group consisting of amide polymers, ethylene/vinyl-acetate copolymers, the copolymer of the first layer, and ionomers;
 - (c) a first core layer comprising an ethylene/vinyl-acetate copolymer;
 - (d) a second core or barrier layer comprising a polymer selected from the group consisting of copolymers of 65 vinylidene chloride and hydrolyzed copolymers of ethylene/vinyl-acetate;

- (e) said core layers being internal film layers positioned between said first and second surface layers;
- (f) at least one adhesive layer to promote adhesion of the barrier layer to another layer; and
- (g) said film comprising at least five layers.
- 2. The film of claim 1 wherein the first surface layer is cross-linked.
- 3. The film of claim 1 wherein the first surface layer comprises a blend of the copolymer defined in (a) (1) and (2) with a copolymer selected from the group consisting of copolymers of ethylene/vinyl-acetate and copolymers of ethylene/butyl-acrylate.
- 4. The film of claim 1 wherein the second core or barrier layer comprises a vinylidene chloride copolymer and the second surface layer comprises a polyamide.
 - 5. A bag formed from the film of claim 1.
- 6. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties, said film comprising:
 - (a) a first surface layer which is heat-sealing, said first surface layer comprising a blend of (i) a linear copolymer of 90% to 75% ethylene and 10% to 25% of an alpha-olefin having 4 to 8 carbon atoms per molecule, said linear copolymer having a density of less than 915 kg/m³ and at least 906 kg/m³, and (ii) up to 50% by weight, based on the total weight of the first surface layer, of a polymer compatible with said linear copolymer selected from the group consisting of linear polyethylene copolymers having a density above 915 kg/m³, low density polyethylene, ethylene vinylacetate, acidmodified ethylene vinylacetate, polypropylene, copolymers of ethylene and propylene, ionomeric polymers and ethylene/alkylacrylate copolymers wherein the alkyl moiety has 1 to 8 carbon atoms; and

12

- (b) a second surface layer comprising a polymer material selected from the group consisting of said linear copolymer of the first surface layer, ethylene-vinylacetate copolymers, polyamides and ionomeric resins.
- 7. A multi-layer, heat-shrinkable thermoplastic packaging 5 film having excellent heat shrink and cold seal properties as recited in claim 6, said film further comprising:
 - (c) a first internal layer between said first surface layer and said second surface layer, said first internal layer comprising a core or barrier material.
- 8. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 7, said film further comprising:
 - (d) a second internal layer between said first internal layer and said second surface polymer layer, said ¹⁵ second internal layer comprising a core or barrier material.
- 9. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 8, wherein said core or barrier materials of said first and second internal layers are selected from the group consisting of copolymers of ethylene vinylacetate and polyvinylidene chloride copolymers.
- 10. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 8, further comprising:
 - (e) an adhesive layer between said first surface layer and said second surface layer.
- 11. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 10, wherein said at least one adhesive layer contains acid-modified ethylene vinylacetate.
- 12. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 8, wherein the core or barrier material of said first internal layer contains a copolymer of ethylene vinylacetate and the core or barrier material of said second internal layer contains polyvinylidene chloride.
- 13. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 12, further comprising:
 - (e) an adhesive layer between said first internal layer and said second internal layer; and
 - (f) an adhesive layer between said second internal layer 45 and said second surface layer.
- 14. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 13, wherein said adhesive layers contain acid-modified ethylene vinylacetate.
- 15. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 7, wherein said first surface layer is cross-linked.

- 16. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 6, wherein in the heat-sealing blend, said polymer compatible with the linear copolymer is selected from the group consisting of copolymers of ethylene viny-lacetate, acid-modified ethylene vinylacetate, copolymers of ethylene and propylene, and ethylene-butylacrylate.
 - 17. A bag formed from the film according to claim 16.
- 18. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties, said film comprising:
 - (a) an inner layer comprising a heat-sealing blend of (i) a linear copolymer of ethylene and x to y % by weight, based on the linear copolymer, of an alpha-olefin having 4 to 8 carbon atoms per molecule, wherein $x=0.5n_C+8$ and $y=1.25n_C+15$ with n_C being the number of carbon atoms in the alpha-olefin, said linear copolymer having a density of less than 915 kg/m³ and at least 906 kg/m³, and (ii) up to 50% by weight, based on the total weight of the heat-sealing inner layer, of a polymer compatible with said linear copolymer selected from the group consisting of linear polyethylene copolymers having a density above 915 kg/m³, low density polyethylene, ethylene vinylacetate, acid modified ethylene vinylacetate, polypropylene, copolymers of ethylene and propylene, ionomeric polymers and ethylene/alkylacrylate copolymers wherein the alkyl moiety has 1 to 8 carbon atoms; and
 - (b) an outer layer comprising a polymer material selected from the group consisting of said linear copolymer of the inner layer, ethylene-vinylacetate copolymers, polyamides and ionomeric resins.
- 19. A multi-layer, heat-shrinkable thermoplastic packaging film having excellent heat shrink and cold seal properties as recited in claim 18, wherein in the heat-sealing blend, said polymer compatible with the linear copolymer is selected from the group consisting of copolymers of ethylene vinylacetate, acid-modified ethylene vinylacetate, copolymers of ethylene and propylene, and ethylene-butylacrylate.
 - 20. A bag formed from the film according to claim 18.
- 21. A thermoplastic multilayer packaging film having superior heat shrink and cold seal properties comprising at least an outer polymer layer and an inner heat sealing layer, said heat sealing layer comprising a linear copolymer of ethylene and x to y % by weight, based on the copolymer, of an alpha-olefin with 4 to 8 carbon atoms per molecule, wherein x=0.5nc+8 and y=1.25nc+15 with nc being the number of carbon atoms in the alpha-olefin, said copolymer having a density of less than 0.915 g/cc and at least 0.906 g/cm³.

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