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(54) **MELANGES ET PROCEDES DE MELANGE DE  
COPOLYMERES OLEFINE/ESTER QUI POSSEDENT UNE  
PLUS GRANDE RESISTANCE AUX CONTRAINTES DE  
FISSURATION ET A LA FATIGUE EN EXTERIEUR,  
ARTICLES FAITS DE CES POLYMERS ET PROCEDES DE  
MOULAGE DE CES ARTICLES**

(54) **BLENDS OF AND METHODS OF BLENDING OLEFIN/ESTER  
COPOLYMERS HAVING IMPROVED ENVIRONMENTAL  
STRESS CRACKING OR ENVIRONMENTAL FATIGUE  
RESISTANCE, PRODUCTS MADE THEREFROM, METHODS  
OF MOLDING SAID PRODUCTS**

(57) Cette invention concerne un mélange et un article flexible se composant de deux copolymères d'un oléfine et d'un monomère d'ester carboxylique non saturé en éthylène. Ces copolymères sont choisis de manière à ce que chacun d'entre eux comprenne plus de 6 % en poids d'un monomère d'ester carboxylique non saturé en éthylène ou, encore, de manière à ce qu'ils représentent plus de 10 % en poids du mélange. Dans le cas où ils possèdent des contenus en ester similaires ou, plus précisément, qui diffèrent de moins de 6 % en poids, les copolymères sont choisis de manière à ce qu'ils présentent une différence, entre leurs flux à l'état fondu, qui soit supérieure à 8 environ. Dans le cas où ils possèdent des contenus en ester non similaires ou, plus précisément, qui diffèrent de plus de 6 % en poids, ces copolymères sont choisis de manière à ce que le rapport entre leurs flux à l'état fondu soit inférieur ou égal à 2 environ.

(57) A blend and flexible product made of two copolymers of an olefin and an ethylenically unsaturated carboxylic ester monomer. The copolymers are selected such that each copolymer includes greater than 6 weight percent ethylenically unsaturated carboxylic ester monomer, or selected to be more than 10 weight percent of the blend. If the copolymers have similar ester contents, that is differing by less than 6 weight percent, the copolymers are selected such that their difference in their melt flows is greater than about 8. If the copolymers have dissimilar ester contents, that is differing by more than 6 weight percent, the copolymers are selected such that the ratio of their melt flows is about 2 or less.





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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US97/05617 <b>(22) International Filing Date:</b> 3 April 1997 (03.04.97)  <b>(30) Priority Data:</b> 60/014,622                      4 April 1996 (04.04.96)              US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventor:</b> O'DONNELL, Hugh, Joseph; 240 Hillcrest Drive, Cincinnati, OH 45215 (US).  <b>(74) Agents:</b> REED , T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> BR, CA, CN, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the  claims and to be republished in the event of the receipt of  amendments.</i>
<b>(54) Title:</b> BLENDS OF AND METHODS OF BLENDING OLEFIN/ESTER COPOLYMERS HAVING IMPROVED ENVIRONMENTAL STRESS CRACKING OR ENVIRONMENTAL FATIGUE RESISTANCE, PRODUCTS MADE THEREFROM, METHODS OF MOLDING SAID PRODUCTS		
<b>(57) Abstract</b> <p>A blend and flexible product made of two copolymers of an olefin and an ethylenically unsaturated carboxylic ester monomer. The copolymers are selected such that each copolymer includes greater than 6 weight percent ethylenically unsaturated carboxylic ester monomer, or selected to be more than 10 weight percent of the blend. If the copolymers have similar ester contents, that is differing by less than 6 weight percent, the copolymers are selected such that their difference in their melt flows is greater than about 8. If the copolymers have dissimilar ester contents, that is differing by more than 6 weight percent, the copolymers are selected such that the ratio of their melt flows is about 2 or less.</p>		

BLEND OF AND METHODS OF BLENDING OLEFIN/ESTER COPOLYMERS  
HAVING IMPROVED ENVIRONMENTAL STRESS CRACKING OR  
ENVIRONMENTAL FATIGUE RESISTANCE, PRODUCTS MADE THEREFROM,  
METHODS OF MOLDING SAID PRODUCTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to blends of copolymers of olefins/and ethylenically unsaturated carboxylic ester monomers having improved environmental stress cracking or environmental fatigue resistance, to methods of making such blends, to products made therefrom, and to methods of molding such products.

2. Description of the Related Art

Stress cracking or environmental stress cracking (ESC) is the brittle failure of plastic parts when simultaneously subjected to mechanical stress and chemical exposure. Environmental fatigue (EF) is the failure or cracking of a part when simultaneously subjected to dynamic mechanical stress and chemical exposure. Insufficient environmental stress cracking or environmental fatigue resistance leads to greatly shortened service life of a part.

Ethylene/vinyl acetate copolymers are commonly injection molded into products utilized in applications requiring good environmental stress cracking or environmental fatigue resistance.

An ethylene/vinyl acetate copolymer with good environmental stress cracking or environmental fatigue resistance is obtained by selecting a high molecular weight viscous resin especially a resin with a narrow molecular weight distribution. Unfortunately, in a process such as injection molding, especially if the mold has small intricate passages, such a viscous resin cannot be molded into a product.

There are numerous patents disclosing polymers having improved environmental stress crack resistance, including: U.S. Patent No. 3,261,889, issued July 19, 1966 to van't Wout, U.S. Patent No. 3,382,298, issued May 7, 1968 to Larsen et al., U.S. Patent No. 3,410,928, issued November 12, 1968 to Baum, U.S. Patent No. 3,485,783, issued December 23, 1969, to Kehe, U.S. Patent No. 3,533,976, issued October 13, 1970, to Eldman, U.S. Patent No. 3,663,663, issued May 16, 1972 to Bernie et al., U.S. Patent No. 3,770,852, issued November 6, 1973 to Hager et al., U.S. Patent No. 3,808,047,

issued April 30, 1974 to McAda, and U.S. Patent No. 4,312,918, issued January 26, 1982 to Bostwick.

However, in spite of these advancements in the prior art, there is still a need for an ethylene/vinyl acetate copolymer blend having improved stress cracking resistance, and methods of making and molding such copolymers.

These and other needs in the art will become apparent to those of skill in the art upon review of this specification, including its drawings and claims.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide for blends of ethylene/vinyl acetate copolymers having improved stress cracking resistance, for products made therefrom, for methods of making the blends, and for methods of forming the products.

These and other objects of the present invention will become apparent to those of skill in the art upon review of this specification, including its drawings and claims.

According to the present invention, there is provided a blend composition of a first copolymer and a second copolymer of an olefin and an ethylenically unsaturated carboxylic ester monomer, with each having greater than 6 weight percent ester monomer content. In an alternative embodiment, the difference between the copolymer monomer contents are less than about 6 weight percent, and the difference between the copolymer melt flow indexes is greater than about 8. In a second alternative embodiment, the difference between the copolymer ester monomer contents is at least 6 weight percent, and the ratio of the melt flow index of the copolymer having a higher ester monomer content to the melt flow index of the other copolymer, is about 2 or less.

According to another embodiment of the present invention there is provided a blend composition of a first copolymer and a second copolymer of an olefin and an ethylenically unsaturated carboxylic ester monomer with each copolymer comprising greater than about 10 weight percent of the blend. In an alternative embodiment, the difference between the copolymer ester monomer contents is less than about 6 weight percent, and the difference between the copolymer melt flow indexes is greater than about 8. In a second alternative embodiment, the difference between the copolymer ester monomer content is at least 6 weight percent, and the ratio of the melt flow index of the copolymer having a higher ester monomer content to the melt flow index of the other copolymer, is about 2 or less.

Another embodiment provides a method of making a polymer blend by generally contacting together, the first and second copolymers as described above.

Even another embodiment provides a product having a body with a flexible portion made of the blend of the first and second copolymer as described above.

Still another embodiment provides a method of forming a product which includes forming a softened or molten blend of first and second copolymers as described above, forming the molten blend into a desired shape, cooling the formed shape to stabilize the product.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of a sprayer bellows 60 of Example 2.

FIG. 2 is a side view of lotion pump bellows 30 of Example 2.

#### DETAILED DESCRIPTION OF THE INVENTION

The blends of the present invention include a first and second copolymer of an  $\alpha$ -olefin and an ethylenically unsaturated carboxylic ester monomer. While preferred, it is not necessary that the copolymers have similar monomers.

The first copolymer is selected to provide the blend with suitable resistance to cracking, while not deterring its use for molding. Therefore, the first copolymer must have a molecular weight low enough to provide suitable flowability for the type of mold utilized. For example, the molding of fine or thin walled parts requires lower molecular weight than the molding of other parts. However, the molecular weight of the first copolymer must also be high enough to provide the desired resistance to cracking. Generally, the first copolymer utilized in the present invention will generally have a melt flow index in the range of about 0.5 to about 35, preferably from about 1 to about 20, more preferably from about 1.2 to about 15, and most preferably from about 1.5 to about 10.

The first copolymer utilized in the present invention will generally have an ester monomer content greater than 6 weight percent, preferably from about 8 to about 40, more preferably from about 10 to about 40, even more preferably from about 12 to about 40, still more preferably from about 20 to about 35, and yet more preferably from about 25 to about 28 weight percent.

The second copolymer utilized in the present invention is selected to provide flowability to the blend, and will generally have a lower molecular weight than the first copolymer. The second copolymer will generally have a melt flow index in the range of

about 3 to about 50, preferably from about 5 to about 40, and most preferably from about 7 to about 35 weight percent.

The second copolymer utilized in the present invention will generally have an ester monomer content greater than about 6, preferably from about 8 to about 22, more preferably from about 10 to about 22, even more preferably from about 12 to about 22, still more preferably from about 15 to about 22, and yet more preferably from about 15 to about 19 weight percent.

In the practice of the present invention, the first and second copolymers are generally selected to provide a blend having a desired resistance to environmental stress cracking and environmental fatigue. As these properties will vary depending upon the particular chemical environment, the selection of the copolymers must be tailored to each environment.

In general, the copolymers can be selected by one of two general embodiments, depending upon whether the comonomer contents of the two copolymers is similar or dissimilar.

For the purposes of this invention, copolymer contents are considered similar if the arithmetic difference (i.e., upon subtraction) in their weight percent ester comonomer contents is generally less than about 6, preferably less than about 4, and most preferably less than about 3 weight percent. For such similar copolymers, the first and second copolymers are chosen such that their melt flow indexes are different. Preferably, the arithmetic difference between the melt flow indexes of the two copolymers is greater than about 8, more preferably greater than about 15, and most preferably greater than about 20.

The second embodiment consists of choosing two copolymers such that the numerical difference (i.e. upon subtraction) between their weight percent comonomer contents is at least 6, more preferably at least about 8, and most preferably at least about 9 weight percent. Preferably, the copolymers utilized with this method comprise in the range of about 5 to about 40, more preferably from about 9 to about 35, and most preferably from about 15 to about 28 weight percent monomer. The resins are chosen so that the ratio of the melt flow index of the copolymer with the higher ester monomer content to the melt flow index of the copolymer with the low ester monomer content is about 2 or less, more preferably about 1.5 or less, and most preferably less than about 1.

The a-olefin utilized in the copolymers of the present invention generally comprises at least 2 carbon atoms, preferably from about 2 to about 8, more preferably from about 2 to about 4, and most preferably from about 2 to about 3 carbon atoms.

Preferable examples of suitable  $\alpha$ -olefins include ethylene, propylene, butylene, most preferably ethylene.

The ethylenically unsaturated carboxylic ester monomers utilized in the copolymers of the present invention are selected from the group of vinyl esters of saturated carboxylic acids and alkyl esters of an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acids. Suitable examples include methyl acrylate, ethyl acrylate, butyl acrylate, isobutyl acrylate, methyl methacrylate, diethyl maleate, dimethyl fumarate, vinyl acetate, vinyl propionate and the like. Preferably the copolymer contains at least one of the following ester monomers: methyl acrylate, ethyl acrylate and vinyl acetate. Most preferably, the copolymer ethylene vinyl acetate.

The blends of the present invention can include any suitable amount of first and second copolymer which provide the desired properties. Generally, in the blends of the present invention the first and second copolymers will each comprise greater than about 10 weight percent of the blend, preferably in the range of greater than about 10 to less than about 90, more preferably from about 12 to about 88, even more preferably from about 15 to about 85, still more preferably from about 20 to about 80, and still even more preferably in the range of about 30 to 70 weight percent of the blend.

The blends of the present invention can be obtained utilizing any suitable blending method and apparatus, for example, Banbury mixers, steam heated two roll mill mixers, screw type extruders, and the like. Any conventional method which provides a homogeneous mixture can be employed. For example, the selected polymers can be fluxed along with any desired additives in a Banbury mixer for a four or five minute cycle and then to work the material on a two-roll mill before transferring it into the rolls of a calender mill. It is also possible to have the mixing accomplished in a mixing extruder prior to forming the composition. The blends can also be formed in one or more reactors *in situ*.

The blends of the present invention will find utility in the making of products subject to static or cyclic loading conditions in a harsh chemical environment, for example, bellows, diaphragms, and boots. Such products have a flexible, resilient, spring-like portion, which can be subject to static or cyclic loading. Such a spring-like portion may comprise one or more folds, pleats or the like, to form an accordion-shaped section which functions as a spring, for example as with a bellows.

Products can be made from the blends of the present invention utilizing any suitable method, including for example, a broad range of polymer fabrication processes such as, injection molding, stamp molding, extrusion, pultrusion, pressing, blow

molding, and the like. Generally, the blends of the present invention are heated above the melting point, formed into a desired shape, and cooled to stabilize the blend into the desired shape.

Methods of copolymerizing an olefin and an ethylenically unsaturated carboxylic ester monomer are well known, and any suitable method may be utilized. The typical method utilizes a high pressure free radical reaction where ethylene and liquid comonomer are admixed in the presence of catalyst to create copolymer. Such reaction may be conducted in a stirred tank reactor as described in U.S. Patent No. 2,220,429, or conducted in a continuous tubular reactor as described in U.S. Patent No. 3,988,509, both herein incorporated by reference.

In the practice of the present invention, there may be utilized, as desired and/or necessary, antioxidants, antiblock agents, slip agents, cross linking agents, stabilizers, ultraviolet ray absorbers, lubricants, foaming agents, antistatic agents, organic and inorganic flame retardants, plasticizers, dyes, pigments, talc, calcium carbonate, carbon black, mica, glass fibers, carbon fibers, aramid resin, asbestos, as well as other fillers as are known in the art.

The blends of the present invention may be further blended with or incorporated into one or more thermoplastics. The first and second copolymers can first be blended and then blended with the one or more thermoplastics, or the one or more thermoplastics can be included during the blending of the first and second copolymers. Suitable thermoplastics include polyolefins, especially polyethylenes and polypropylenes, polyesters, polyacrylamides, polyamides, polycarbonates, polyurethanes, polyacrylonitriles, and butadiene styrenes. Preferred polyethylenes include linear low density polyethylenes.

## EXAMPLES

### Example 1

Blends of commercially available resins were prepared as follows. Desired portions of resins were dry blended to obtain a dispersion. Dry blending was performed in a Kelly Duplex mixer sold by Duplex Mill & Manufacturing Company, Springfield OH 45501. The resin was blended for 10 to 20 minutes. Next, the dry blended resins were feed to the hopper of an extruder for melt blending. The extrusion was performed in a 30 mm Werner Pfleiderer ZSK-30 corotating twin screw extruder, made in Austria, configured with one kneading section. The temperatures in the feeding zone were



approximately 130°C, and the temperatures in the plasticizing and mixing zones of the barrel were approximately 170°C, with melt temperature measured at the die at about 175°C. Screw speed was about 250 rpm, and the throughput was between 20 and 50 pounds per hour. A two hole die plate which created dual strands of molten plastic was utilized. Strands were quenched in 50 to 70°F water and pelletized.

Some of the blends made by the method above are listed in Table 1. Ethylene vinyl acetate resins used in the blends were either Ultrathene (UE) obtained from Quantum Chemical Co., Cincinnati OH or Elvax (EL) obtained from E.I. DuPont, Wilmington DE. Blends made from resins with a range of vinyl acetate contents between 9 and 28 percent and MFI between 1.8 and 43 were evaluated. The estimated VA, MFI, and MFI ratio are listed in the last three columns of Table 1.

Table 1. Prepared Blends of EVA Resins

Blend	Resin A	VA (%)	MFI (g/10min)	Resin B	VA (%)	MFI (g/10min)	Ratio A:B (wt.%)	VA (est. %)	MFI (est.)	MFI Ratio
1	UE634-000	28	3	UE652-059	19	30	5:95	19	27	0.1
2	EL240	28	43	UETR209	15	23	35:65	20	29	1.9
3	UE652-059	19	30	UE630-000	17	1.8	50:50	18	8	16
4	EL250	28	25	EL760	9	2	50:50	19	7	12
5	UE634-000	28	3	UE652-059	19	30	40:60	23	12	0.1
6	EL250	28	25	UE635-000	9	10	85:15	25	22	2.5
7	EL260	28	6	UE635-000	9	10	85:15	25	7	0.6

Example 2

Both commercially available neat resins and blended resins as described in Example 1 were injected molded into a spring like bellows illustrated in FIGs. 1 and 2. The commercial resins are listed in Table 2-A.

Table 2-A. Commercial Resins Molded Into Bellows

Material	Resin	VA (%)	MFI (g/10min)
A	UE630-000	17	1.8
B	EL450	18	8
C	UE652-059	19	30
D	UE634-000	28	3
E	EL250	28	25
F	EL260	28	6

Method A: The bellows 60 illustrated in Figure 1 (sprayer bellows) was made in a hand-mold lacking temperature control or cooling circuits. Because of manual handling, the cooling time of the part and residence time in the injection molder were variable. The injection molder used for manufacture of this style bellow was an Arburg Allrounder 220-75-250, made in Germany. The melt temperature measured in these runs was between 195 and 225°C. An injection time between 0.2 and 0.6 seconds was used to fill the part. A pressure of about 12,000 psi was used to pack the part and this pressure was held for about 2 seconds. Bellows were removed from the core side of the mold by inflating the bellows with an air pressure of about 25 psi while simultaneously pulling the bellow off the core.

Method B: The bellows 30 illustrated in Figure 2 (lotion pump bellows) were made in an automatic unit cavity mold. The injection molding machine was a Engel 200 ton tie-barless machine, model EC88, made in Canada. Manufacturing

conditions are specified in Table 2-B, and are similar to the conditions used to manufacture the bellows described in Method A. Producing a bellow in the automatic mold with the Engel injection molding machine allowed for a more uniform and reproducible operation, in particular control of time, pressure, and temperature.

Table 2-B. Typical Injection Molding Parameters

Parameter	Setting	Units
Melt Temperature	195-225	°C
Screw RPM	200-400	rpm
Back pressure	20-60	psi
Injection Time	0.5-0.7	s
Hold Pressure	5000-8000	psi
Hold Time	2-6	s
Cooling Time	8-12	s
Mold Temperature	90	°C

### Example 3

Bellows made from blends of Materials A, C, and D as described in Table 2-A, and by method 2A of Example 2 were subjected to cycle testing (2Hz, 5/8" stroke, 10,000 strokes) in commercially available Comet Bathroom Cleaner. Results are presented in Table 3.

Table 3

Bellows material (percentage ratio)	Results
C (100)	Substantial crazing throughout bellows.

A/C (70/30)	Some minor crazing in apex.
A/C (85/15)	Only one crack with some crazing.
C/D (60/40)	Some crazing in inner apex.
C/D (95/5)	One of two bellows had a large crack, considered a failure.

#### Example 4

The effect on ESCR of a linear low density polyethylene (LLDPE) as a component in an EVA blend was examined. Blend 5 of Table 1 was compared to a ternary blend of Material C and D from Table 2-A and a linear low density polyethylene, GA564, sold by Quantum Chemical Company. These three materials were blended as described in Example 1 in ratios of 55:37:8 percent. The ratio of Material C to D was equal to that of Blend 5. These materials were molded into bellows as described in Method A of Example 2 and tested for ESCR in the manner described in Example 5. The chemical environment for these tests consisted of cleaning solutions sold commercially as Comet Pine Bathroom Cleaner, Comet Mildew Stain Remover, and Spic and Span Cinch Glass & Surface Cleaner (Cinch) by Procter & Gamble Co. The Comet Pine is an acidic aqueous solution of pH 4, in part, containing dipropylene glycol butyl ether, citric acid and perfume. The Comet Mildew Stain Remover is an aqueous cleaning solution of pH 13, in part containing sodium hypochlorite or bleach. The Cinch is an alkaline aqueous cleaning solution of pH 11, in part, containing isopropanol and perfumes.

A total of three bellows were tested and the average time to failure was reported in Table 4. The inclusion of LLDPE, GA564, in the ternary blend did not diminish the ESCR relative to blend 5.

Table 4. Time To Failure in Modified ESCR Test With Bellows in Cleaners (hrs.)

Resin	Comet Pine	Comet Mildew	Cinch
Material C	2	1	1
Material A	>72	64	5
Material D	6	>72	>72
Blend 5	26	55	40
UE652/UE634/GA564 (55/37/8%)	35	41	42

Example 5

Bellows made as described in Example 2 were compressed to 0.7" and placed in Comet Bathroom Cleaner, the first hour at room temperature, 100°F thereafter, and subsequently observed for the detection of cracking. Results are presented in Table 5.

TABLE 5  
ENVIRONMENTAL STRESS CRACKING RESISTANCE  
HOURS TO FORMATION OF SMALL CRACKS/HOURS TO FORMATION OF  
LARGE CRACKS(FAILURE)

Material\Sample No.	I	II	III	Average
UE 634 (100%)	23	23	23	23
ELVAX 460	23	26.5	8	19.2
UE662 (100%)	1	1/2	1	1/2

Example 6

Materials listed in Table 2-A individually or in blends prepared as described in Example 1 were made into bellows as described in Method B of Example 2. The environmental fatigue of these materials was tested as described in Example 3 with the exception that the stroke length was ½". These materials cover a vinyl acetate range from 18 (low) to 28% (high). Blends were prepared by mixing low and high vinyl acetate containing resins. These materials were tested in Pantene Shampoo as sold in Japan. This shampoo was found to be representative of other shampoos in terms of the aggressiveness of the formula as a stress cracking agent. The bellows were tested within a four week period of manufacture. The results are shown in Figure 3. The ordinate measures the degree of failure on a scale from 1 to 6. A minor amount of cracking (less than 15 small cracks) is indicated by a crack index of 2. The other crack indices are repressed by the following conditions: 1- no cracking; 3 - more than 15 small cracks without any deep cracks; 4 - deep cracks potentially leading to a hole; 5 - one or more isolated holes; 6 - coalescence of two or more holes typically forming a slit. The abscissa measures the amount of either Material B or Material C in the blend (i.e. the low vinyl acetate resin): the remainder of the blend being composed of Materials D, E, or F (containing a high amount of vinyl acetate) as indicated in the key of Figure 3. The MFI for each material is also shown in the key of Figure 3.

The MFI for the five blends of Figure 3 at a 60% composition are shown in Table 6-A. Resistance to cracking increases with either a decrease in MFI or a decrease in MFI ratio.

Table 6-A. MFI for Blends in Figure 3 Having a 60% Composition.

Materials	Crack Index	MFI (est.)	MFI Ratio Hi:Lo
C:E	3	29	0.8
B:E	3	13	3.1
C:F	2.5	16	0.2

C:D	2.25	12	0.1
B:F	1.75	7	0.8

The approximate compositions (based on the b-spline fit) where the Crack Index equals 2 are listed in Table 6-B, along with estimated MFI and MFI Ratios. From this data, it is clear that EVA compositions with greater percentages of a low vinyl acetate EVA can achieve satisfactory crack resistance if the blends have lower MFI (<20) or lower MFI ratio (<1).

Table 6-B. Blends From Figure 3 Having Crack Index Equal To 2

Materials	Composition	Estimated MFI	MFI Ratio Hi:Lo
C:E	30:70	26	0.8
B:E	30:70	18	3.1
C:F	45:55	12	0.2
B:F	60:40	7	0.8

#### Example 7

The blends of Example 6 were tested for environmental fatigue resistance in a commercial cleaning product, Comet Pine Cleaner made by the Procter & Gamble Co. This product was described in Example 5. The environmental fatigue resistance was graded on a scale from 1 to 6 as described in Example 6. This scale shown on the ordinate and abscissa of Figure 4 are as described in Example 6. The MFI for each material is also shown in the key of Figure 4.

The MFI for the five blends presented in Figure 4 at a 60% composition are shown in Table 7-A. The resistance to cracking increases with either a decrease in MFI or a decrease in MFI ratio.



Table 7-A. MFI for Blends in Figure 4 Having a 60% Composition.

Materials	Crack Index	MFI (est.)	MFI Hi:Lo	Ratio
C:E	3.8	29	0.8	
B:E	3.0	13	3.1	
C:F	2.0	16	0.2	
B:F	2.0	7	0.8	
C:D	1.0	12	0.1	

The approximate compositions (based on the b-spline fit) where the Crack Index equals 2 are listed in Table 7-B, with estimated MFI and MFI Ratio also listed. From this data, it is clear that compositions with greater percentages of a low vinyl acetate EVA can achieve satisfactory crack resistance if the blends have lower MFI (<20) or lower MFI ratio (<1).

Table 7-B. Blends From Figure 4 Having Crack Index Equal To 2

Materials	Compositio n	Estimated MFI	MFI Hi:Lo	Ratio
C:E	20	26	0.8	
B:E	20	18	3.1	
C:F	50	12	0.2	
B:F	60	7	0.8	
C:D	80	12	0.1	

Example 8

The blends prepared in Example 6 were tested for environmental fatigue resistance in a commercial cleaning product, Tide made by the Procter & Gamble Co. This product was, in part, comprised of anionic and nonionic surfactants, enzymes, and fragrances. The environmental fatigue resistance was graded on a scale from 1 to 6 as described in Example 6. This scale shown on the ordinate and abscissa of Figure 5 are as described in Example 6. The MFI for each material is also shown in the key of Figure 5.

The MFI for the five blends of Figure 5 at a 60% composition are shown in Table 8-A. The resistance to cracking increases with either a decrease in MFI or a decrease in MFI ratio.

Table 8-A. MFI for Blends in Figure 5 Having a 60% Composition.

Materials	Crack Index	MFI (est.)	MFI Ratio Hi:Lo
C:E	4.0	29	0.8
B:E	3.3	13	3.1
C:F	3.0	16	0.2
B:F	2.3	7	0.8
C:D	2.0	12	0.1

The approximate compositions (based on the b-spline fit) where the Crack Index equals 2 are listed in Table 8-B, along with estimated MFI and MFI Ratios. From this data, it is clear that compositions with greater percentages of a low vinyl acetate EVA can achieve satisfactory crack resistance if the blends have lower MFI (<20) or MFI ratio (<1).

Table 8-B. Blends From Figure 5 Having Crack Index Equal To 2

Materials	Composition	Estimated MFI	MFI Hi:Lo	Ratio
C:E	0	26	0.8	
B:E	10	18	3.1	
C:F	35	12	0.2	
B:F	50	7	0.8	
C:D	60	12	0.1	

Example 9

Blend 1 and 5 were molded into bellows as described in Method A of Example 2. These materials are 5:95 and 40:60 ratios of Materials D and C, respectively. Material C was also molded into bellows as described in Method A of Example 2. The environmental fatigue resistance of these three bellows was tested as described in Example 3. The results for testing in Comet Bathroom Cleaner are shown in Table 9. Comet Bathroom Cleaner has a pH of 3, and is partially composed of dipropylene glycol butyl ether, citric acid, and perfume.

Table 9. Environmental Fatigue In Comet Bathroom Cleaner

Resins	Crack Index
Blend 1	3
Blend 5	2
Material C	4

Bellows made from Blend 5 are superior to the other bellows. However, even a 5% addition of Material D improves the environmental fatigue resistance of

Material C while a much higher modification, i.e. 40%, is required for the bellows to exhibit significantly improved EFR.

#### Example 10

Blends 6 and 7, containing 85% of either Material E or Material F, were molded into bellows as described in Method B of Example 2. Materials E and F were also molded into bellows as described in Method B of Example 2. The environmental fatigue resistance of these four bellows was tested as described in Example 3, with results shown in Table 10.

Table 10. Environmental Fatigue of Bellows Made from Materials E and F

Resin	Pantene	Comet Pine	Tide (drop column)
Blend 6	2.5	2.0	2.0
Blend 7	1.5	1	1.0
Material E	1.0	1	2.0
Material F	1.0	1	1.3

Bellows made from Materials E and F exhibit no cracking or failure after environmental fatigue testing. The addition of 15% UE635-000 (listed in Table 1) to these materials deteriorates the EFR of the blend little to none in comparison to the neat resins. The blend conforming to the preferred embodiment is blend 7. The performance of this blend, that contains 85% of Material F, is equal to that of Material F. The blend not conforming to the preferred embodiment is blend 6. It performs slightly worse than Material E which comprises 85% of Blend 6.

#### Example 11

Blends 3 and 4 as listed in Table 1, of either 18 or 19% vinyl acetate with similar MFI but different MFI ratios were made into bellows as described in Method B of Example 2 and were tested for environmental fatigue. Blend 3 and Blend 4

have estimated MFI ratios of 8 and 7, respectively. Also tested was a commercial resin, Material B, containing 18% vinyl acetate and having a similar MFI to the blends. The results of environmental fatigue are listed in Table 11.

Table 11. Environmental Fatigue of Blended Bellows vs. Material B

Resin	Pantene	Comet Pine	Tide
Blend 3	1.0	1.0	1.5
Blend 4	2.0	2.5	2.0
Material B	2.8	3	3.0

These three resins have similar %VA and MFI, however, the environmental fatigue of the three resins is distinctly different. The environmental fatigue of the blends is superior to the unblended Material B. Of the blends, Blend 3, which conforms to the preferred embodiment, has superior environmental fatigue.

#### Example 12

Another comparison of a blended resin to an unblended commercial resin is examined. Blend 2 contains 20% vinyl acetate and has a MFI of 29. This blend is compared to Material C of Table 2-A which has similar properties. These resins were made into bellows by Method B of Example 2, and were tested for environmental fatigue as by Example 3.

Table 12. Environmental Fatigue of Blended Bellows vs. Material C

Resin	Pantene	Comet Pine	Tide
Blend 2	3.3	4.0	3.0
Material C	3.0	4.8	4.0

The results shown in Table 12 indicate that Blend 2, which does not conform to the preferred embodiment, performs equally or somewhat superior to the unblended Material C.

While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which this invention pertains.

1. A blend composition comprising:

(a) a first copolymer of a first olefin and a first ethylenically unsaturated carboxylic ester monomer, the copolymer having a first melt flow index and a first weight percent ester monomer content; and

(b) a second copolymer of a second olefin and a second ethylenically unsaturated carboxylic ester monomer, the copolymer having a second melt flow index and a second weight percent ester monomer content,

wherein the first copolymer and the second copolymer each comprise greater than 6 weight percent ethylenically unsaturated carboxylic ester monomer.

2. A blend composition comprising:

(a) a first copolymer of an olefin and an ethylenically unsaturated carboxylic ester monomer, the copolymer having a first melt flow index and a first weight percent ester monomer content; and

(b) a second copolymer of the olefin and the ethylenically unsaturated carboxylic ester monomer, the copolymer having a second melt flow index and a second weight percent ester monomer content,

wherein the first copolymer and the second copolymer each comprise greater than about 10 weight percent of the blend composition.

3. A method of making a blend composition, the method comprising contacting together:

(a) a first copolymer of a first olefin and a first ethylenically unsaturated carboxylic ester monomer, the copolymer having a first melt flow index and a first weight percent ester monomer content; with a

(b) a second copolymer of a second olefin and a second ethylenically unsaturated carboxylic ester monomer, the copolymer having a second melt flow index and a second weight percent ester monomer content,

wherein the first copolymer and the second copolymer each comprise greater than 6 weight percent ethylenically unsaturated carboxylic ester monomer.

4. A method of making a blend, the method comprising contacting together:

(a) a first copolymer of a first olefin and a first ethylenically unsaturated carboxylic ester monomer, the copolymer having a first melt flow index and a first weight percent ester monomer content; with a

(b) a second copolymer of a second olefin and a second ethylenically unsaturated carboxylic ester monomer, the copolymer having a second melt flow index and a second weight percent ester monomer content,

wherein the first copolymer and the second copolymer each comprise greater than about 10 weight percent of the blend composition.

5. A product comprising a body having a flexible portion, the flexible portion comprising:

(a) a first copolymer of a first olefin and a first ethylenically unsaturated carboxylic ester monomer, the copolymer having a first melt flow index and a first weight percent ester monomer content; and

(b) a second copolymer of a second olefin and a second ethylenically unsaturated carboxylic ester monomer, the copolymer having a second melt flow index and a second weight percent ester monomer content,

wherein the first copolymer and the second copolymer each comprise greater than 6 weight percent ethylenically unsaturated carboxylic ester monomer.

6. A product comprising a body having a flexible portion, the flexible portion comprising:

(a) a first copolymer of an olefin and an ethylenically unsaturated carboxylic ester monomer, the copolymer having a first melt flow index and a first weight percent ester monomer content; and

(b) a second copolymer of the olefin and the ethylenically unsaturated carboxylic ester monomer, the copolymer having a second melt flow index and a second weight percent ester monomer content,

wherein the first copolymer and the second copolymer each comprise greater than about 10 weight percent of the flexible portion.

7. A method of making a product, the method comprising

(a) heating above its melting point to form a molten mixture, a blend of:

(i) a first copolymer of a first olefin and a first ethylenically unsaturated carboxylic ester monomer, the copolymer having a first melt flow index and a first weight percent ester monomer content; with a

(ii) a second copolymer of a second olefin and a second ethylenically unsaturated carboxylic ester monomer, the copolymer having a second melt flow index and a second weight percent ester monomer content,

wherein the first copolymer and the second copolymer each comprise greater than 6 weight percent ethylenically unsaturated carboxylic ester monomer,

(b) forming the molten mixture into a desired shape;



(c) cooling the shape below its melting point.

8. A method of making a product, the method comprising

(a) heating above its melting point to form a molten mixture, a blend of:

(i) a first copolymer of a first olefin and a first ethylenically unsaturated carboxylic ester monomer, the copolymer having a first melt flow index and a first weight percent ester monomer content; with a

(ii) a second copolymer of a second olefin and a second ethylenically unsaturated carboxylic ester monomer, the copolymer having a second melt flow index and a second weight percent ester monomer content,

wherein the first copolymer and the second copolymer each comprise greater than about 10 weight percent of the flexible portion.

(b) forming the molten mixture into a desired shape;

(c) cooling the shape below its melting point.

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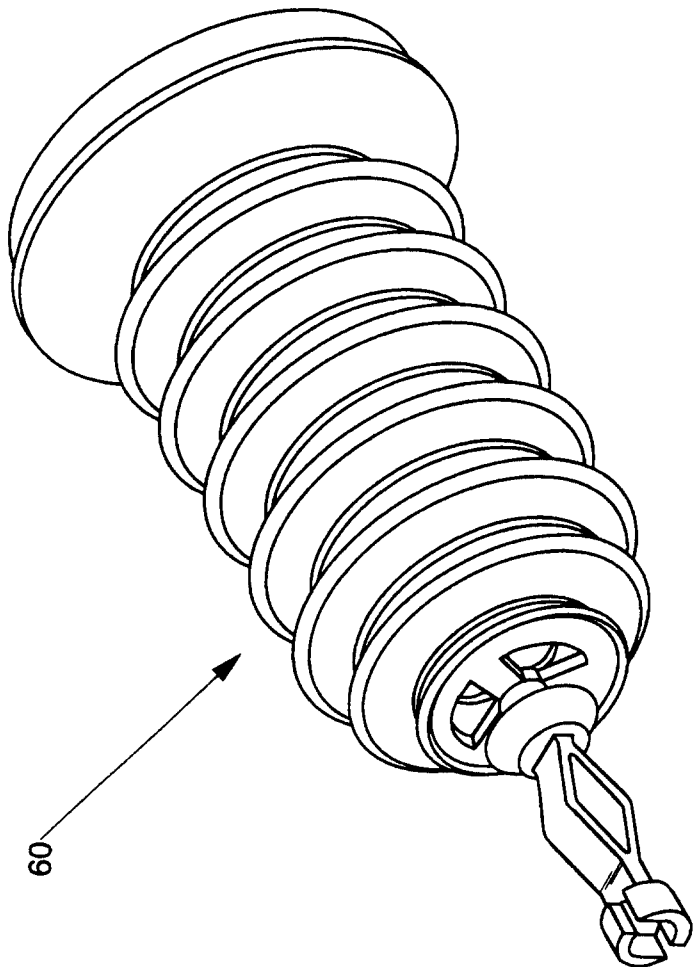


Fig. 1

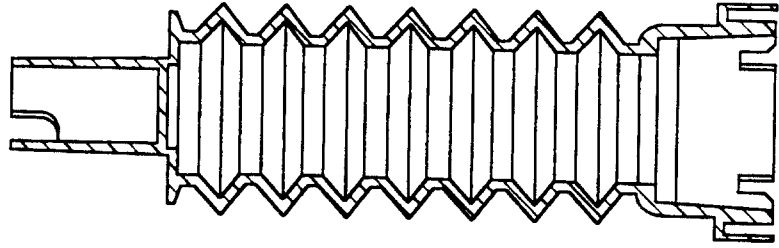


Fig. 2

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