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<p>(21) International Application Number: PCT/US81/01563 (22) International Filing Date: 24 November 1981 (24.11.81) (31) Priority Application Number: 212,645 (32) Priority Date: 3 December 1980 (03.12.80) (33) Priority Country: US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: LEFEVRE, Lloyd, Edward ; 3743 Boy Scout Road, Bay City, MI 48706 (US). STEVENSON, Fred ; 2658 Blades Street, Beaverton, MI 48612 (US).</p>		<p>(74) Agent: JUHL, Nis, H.; The Dow Chemical Company, P. O. Box 1967, Midland, MI 48640 (US). (81) Designated States: AU, CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, NL (European patent), SE (European patent). Published <i>With international search report.</i></p>
<p>(54) Title: EXTRUSION-GRADE VINYLIDENE CHLORIDE COPOLYMER COMPOSITIONS AND FILMS PREPARED THEREFROM</p>		
<p>(57) Abstract</p> <p>A vinylidene chloride copolymer composition manufactured by the addition of a polymeric blend of a grease copolymer, such as low molecular weight ethylene-vinyl-acetate copolymer, with a conventional plasticizer to improve processing of the composition during mixing and extrusion of the composition as a thin film.</p>		

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EXTRUSION-GRADE VINYLIDENE CHLORIDE COPOLYMER
COMPOSITIONS AND FILMS PREPARED THEREFROM

This invention relates in general to extrusion-
-grade vinylidene chloride copolymer compositions and,
additionally, to films prepared therefrom.

While many different materials, e.g., waxed
5 papers, plastic coated papers, aluminum foil, and
polyethylene film are used as protective wrapping,
vinylidene chloride copolymer films are most widely
used because of their low water and gas vapor trans-
mission properties and resistance to mechanical and
10 chemical deterioration as well as their adaptability to
microwave cooking. In many instances, however, the
vinylidene chloride copolymer film does not have suf-
ficient cling and cohesion properties to adhere to
itself when a small amount of pressure is applied as in
15 household applications and, therefore, often does not
adequately seal-in flavor, moisture, and other desirable
properties of fresh or prepared food items.

Accordingly, various additives are frequently
incorporated into the vinylidene chloride copolymer
20 compositions from which film is made in order to increase



the cling properties of the resulting film. In the case of extrusion grade vinylidene chloride copolymer compositions, for example, such additives are frequently in the form of liquids, such as citric acid esters, which typically perform the dual function of a cling enhancer as well as a plasticizer or extrusion aid.

Although the aforementioned additives have been useful in imparting cling properties to vinylidene chloride copolymer films containing them, such additives have introduced new problems. For example, the liquid cling additives have limited solubility in the vinylidene chloride copolymer resin and will sometimes exude to the surfaces of the film and excessively plate-out on, or transfer to, contacting members of film-making or film-handling machinery, thereby causing irregularities in the operation of such machinery or in the quality of the product.

Known additives are also incapable of providing high-cling properties while maintaining a balance of other physical properties. Although high-cling properties, which are required in films used for industrial and consumer applications, can be achieved with the known additives by increasing the amount thereof, such increased cling is attended by a loss of good processability and handleability. Either the films cling too much to themselves and present severe problems in handling because they cannot readily be pulled apart, (i.e., "a blocking" effect), or they are readily handleable but exhibit poor cling properties. In addition to the handleability problems effected by increasing the amount of such additives, other deleterious properties,

such as increased oxygen permeability and cost, as well as decreased modulus of the film, tend to occur.

Accordingly, it is desirable to provide an extrusion grade vinylidene chloride copolymer composition capable of producing a film having inherent cling properties sufficient to enable it to form a seal upon the application of a small amount of pressure, yet which seal can be readily pulled apart. Furthermore, it would be desirable to provide such a high-cling/-low-blocking film wherein the aforementioned problems of high oxygen permeability and cost, and decreased modulus are not as pronounced as in the past. It is also advantageous to provide such a composition having low vinylidene chloride and vinyl chloride residuals and low exudation of such additives over a period of time, which is easy to extrude and relatively inexpensive, has high-cling and is relatively stiff. This invention provides such a novel composition.

The present invention resides in a high cling film comprising an extrudable resin composition comprising:

- (a) a vinylidene chloride copolymer in which a major proportion of the copolymer is a vinylidene chloride monomer with a minor proportion of at least one other polymeric comonomer, and
- (b) less than 10 percent by weight of total resin composition of a polymer blend comprising a grease copolymer having a peak molecular weight of from 500 to 7500 as determined by gel permeation chromatography and a non-polymeric ester plasticizer.

Vinylidene chloride copolymers (Saran®) which can be used in the practice of this invention are any copolymers which are obtained by copolymerizing a major proportion of vinylidene chloride monomer with at least one other comonomer and which are capable of forming a film product under extrusion conditions. Typically, such extrusion grade vinylidene chloride copolymers are crystalline in the normal state and contain from 70 to 95 weight percent of vinylidene chloride, with the remainder comprising one or more ethylenically unsaturated comonomers, such as vinyl chloride, vinyl acetate, vinyl propionate, acrylonitrile, alkyl and aralkyl (butyl) acrylates and methacrylates having alkyl and aralkyl groups of up to about 8 carbon atoms, acrylic acid, acrylamide, vinyl alkyl ethers, vinyl alkyl ketones, acrolein, allyl esters and ethers, butadiene, chloroprene and others. Representative ternary compositions which may be used include the polymers of vinylidene chloride with, for example, acrolein and vinyl chloride; acrylic acid and acrylonitrile; alkyl acrylates and alkyl methacrylates; acrylonitrile and butadiene; acrylonitrile and itaconic acid; acrylonitrile and vinyl acetate, vinyl propionate, or vinyl chloride; alkyl esters or ethers and vinyl chloride; butadiene and vinyl acetate, vinyl propionate, or vinyl chloride; and vinyl ethers and vinyl chloride. Quaternary and higher polymers of similar monomeric compositions, as well as blends of vinylidene chloride copolymers, may also be used advantageously.

The vinylidene chloride copolymers can be made by any manner suitable for preparing extrusion

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grade resins of such copolymers such as by polymerization in mass or in an aqueous medium through the techniques of suspension or emulsion polymerization.

Grease copolymers suitable for use as a cling enhancing additive with the vinylidene chloride copolymers of this invention are generally characterized as greases or oils. Typically, such grease copolymers have peak molecular weights, as determined by gel permeation chromatography, in the range from 500 to 7500, preferably from 1000 to 4000. Gel permeation chromatographic methods for determining molecular weights of polymers are described by J. C. Moore in the J. Polymer Sci. A., 2, 835 (1964). See also L. H. Tung, J. Appl. Polymer Sci., 10, 345 (1966) and W. N. Smith, J. Appl. Polymer Sci., 11, 639 (1967). Since such copolymers have melt flow rates above those which can be accurately measured by ASTM D-1238-70(E) at 190°C and 2.16 kilograms, it is necessary to alter some of the conditions of this test method in order to obtain more meaningful values. Using the apparatus and procedures of ASTM D-1238-70(E) except that the diameter of the plastometer orifice is reduced to 0.50 ± 0.005 mm and the test temperature is 80°C, the grease copolymers utilized in this invention exhibit melt flow rates in the range from 5 to 50, preferably from 10 to 25, decigrams/minute (dg/min).

The low molecular weight or grease copolymers can be prepared by polymerizing the corresponding monomers at high temperatures and pressures in the presence of a free radical catalyst. While forming the grease copolymer is not part of this invention, a suitable means of preparation is described in U.S. Patent 2,395,381 except that higher temperatures and increased



catalyst concentration are used. In a preferred method up to about 20 weight percent based on the total comonomer weight of a telomer such as ethylene or propylene is added to the polymerization zone to inhibit the formation of high molecular weight copolymers.

Preferred grease copolymers of ethylene and vinyl acetate ("EVA") which can be used generally comprise from 10 to 55 weight percent, preferably from 35 to 50 weight percent vinyl acetate, including the partially hydrolyzed derivatives thereof. Minor amounts of other copolymerizable monomers can also be included in the copolymer, so long as they do not deleteriously affect the properties thereof.

The amount of a polymeric blend of the grease copolymer with a conventional plasticizer to be added to the extrusion grade vinylidene chloride copolymer will depend upon the degree of cling properties and stiffness desired in the film product. Generally, the proportion of the grease copolymer/plasticizer blend is from an effective cling-enhancing amount to about 10, preferably from 0.1 to 7, and most preferably from 3.0 to 7.0 weight percent of the extrusion grade composition. This use of less than 10 weight percent of the copolymer blend achieves the desired results without adversely affecting the essential visual characteristics, i.e., the clarity, of the film product. The actual amount required to achieve the desired cling properties will vary with molecular weight of the grease copolymer and the proportion of ester comonomer in the copolymer.

The most desirable embodiments of the present invention comprehend a blend of a conventional plasticizer

with the grease copolymer since a 100 percent application of the grease copolymer can result in handling or processing difficulties because of the tackiness of the grease copolymer. In a blend of the grease copolymer and plasticizer, as the amount of grease copolymer decreases with respect to the amount of the plasticizer, the modulus or stiffness of the film has been found to decrease significantly. This relationship is demonstrated in the Examples in the Table I.

The examples in Table I were conducted with an ethylene/vinyl acetate grease copolymer/plasticizer blend comprising between 3 to 6 percent of the entire composition. The composition also included from 1.0 to 1.5 percent by weight of a stabilizer of an epoxidized soy bean oil (9-62). The plasticizers blended with the EVA grease copolymer were selected from Citroflex® A-4, a citric acid (non-polymeric) ester di-octyl adipate (DOA), and di-iso butyl adipate (DIBA). Actual numbers in Table I show a decrease in modulus as the ratio of conventional plasticizer is increased in proportion to the EVA grease copolymer. Table I illustrates the effect of increasing the percentage of EVA grease copolymer to the plasticizer. As the amount of the plasticizer is decreased and the EVA grease copolymer increased, the modulus increases.

A ratio of from 20 percent plasticizer to 80 percent EVA grease copolymer and from 80 percent plasticizer to 20 percent grease copolymer essentially alleviates any handling and processing difficulties as compared to using 100 percent EVA grease copolymer yet still provides a film having an exceptionally high modulus of greater than about 5300 kg/cm². Thus, an

economical vinylidene chloride copolymer film with the desired stiffness and processability was achieved with the plasticizing component in the composition being an EVA grease copolymer/plasticizer blend of the type
5 hereinbefore described. It will be recognized, however, that as the percentage of the plasticizer increases with respect to the EVA grease copolymer, stiffness is sacrificed.

Where needed or desired, conventional additives
10 may be included with the extrusion grade composition, such as heat stabilizers and the like. Antioxidants, such as those used with conventional cling additives, have not been found to be necessary for the grease copolymers used in the present invention. If desired,
15 however, a minor amount of such materials may be used.

Mixing of the extrusion grade vinylidene chloride copolymer with a grease copolymer/plasticizer blend, plus other additives, if any, can be carried out in conventional resin blending processes and equipment,
20 such as homogenizing blenders or possibly mixing extruders. It is advantageous that all components be as thoroughly mixed as possible so as to improve the cling efficiency contributed by the low molecular weight grease copolymer. Due to the viscous nature of the grease copolymer
25 additive, it is particularly advantageous for thorough mixing that the low molecular weight copolymer be slightly heated before being mixed with the vinylidene chloride copolymer. With a grease copolymer/conventional plasticizer blend, heating may be optional. Although
30 not the only method, a most beneficial and convenient method of obtaining thorough mixing comprises adding the grease copolymer/conventional plasticizer blend to

the polymerization reactor with the monomers used to prepare the vinylidene chloride copolymer. In larger reactors used for polymerization in an aqueous medium, however, care should be taken to avoid adding the
5 grease copolymer/plasticizer blend after the dispersion of monomers has been formed, since such could create a layer of copolymer on the surface of the aqueous medium which would later interfere with the addition of a polymerization terminator, as such is frequently prac-
10 ticed in the art.

Compositions of the vinylidene chloride copolymer and low molecular weight grease copolymer/-plasticizer blends, prepared by any of the aforementioned variations, can be formed into a thin film by
15 any of the conventional methods known for making films from vinylidene chloride copolymers, such as by the cast film process or the trapped bubble/blown film process. Films made in accordance with this invention range in thickness from 0.2 mil (0.0051 mm) to 3.0 mil
20 (0.076 mm), preferably from 0.4 mil (0.0102 mm) to 1 mil (0.0254 mm).

The examples in the following Tables illustrate the invention but are not to be taken as limiting its scope. In the examples, parts and percentages are
25 by weight unless otherwise indicated.

Films were tested for cling by a method consisting of preparing a first portion and a second portion of the film to be tested, both portions having dimensions of 12.7 cm by 20.3 cm. The first portion is
30 then secured lengthwise, i.e., by taping the ends, to the upper surface of a metal plate which is inclined



30° from horizontal and securely mounted on a top-loading balance. The second portion of film is then superimposed upon the first in a face-to-face relationship and the uppermost edge of the second portion is secured by
5 taping leaving the lowermost edge of the second portion free. It is essential that the portions be superimposed without wrinkles, creases, or bubbles. The lowermost, free edge of the second portion is then clamped and attached to a wire hanger, which is in turn attached to
10 the bottom of a movable cart. The cart travels by a system of pulleys and motor upon a raised, inclined track in such fashion that the free end of the second portion of the film will be pulled upward away from the first portion in a continuous vertical direction,
15 thereby peeling or separating the two portions of film so as to propagate the peeled front at a constant rate of 12.7 cm per minute. The average force (in grams) required to separate the two portions is then read from the balance.

20 Block, which is essentially long-term cling, is measured by carefully removing intact two superimposed film portions from a roll of film which had been aged more than one week, and then determining the force required to separate the film portions in a manner
25 similar to that used for measuring cling.

Runs were made comparing the physical characteristics of films prepared by blending from 3 to 6 percent by weight of an ethylene vinyl-acetate grease copolymer/plasticizer blend to a vinylidene chloride
30 copolymer, with varying amounts of the EVA grease copolymer with respect to the plasticizer. The ratio of grease copolymer to plasticizer ranged from as high

as 80 percent of the blend to as low as 20 percent.
All films were aged for a period of 30 days prior to
testing for cling, block and 2% Secant Modulus
by the aforementioned procedure.

TABLE I

Run No.	EVA-Grease Copolymer (%)	Plasticizer (%)	Cling (grams)	Block (grams)	2% Secant Modulus kg/cm ²	2% Secant Modulus psi
1	1.0	2.0	5.5	8.0	7698	109,500
2	2.0	1.0	5.0	7.0	8626	122,700
3	2.0	2.0	7.0	9.5	6608	94,000
4	2.0	2.0	6.5	8.0	7241	103,000
5	2.0	3.0	8.0	9.5	6165	87,700
6	2.5	2.5	8.5	9.0	6404	91,100
7	3.0	2.0	8.0	10.0	6165	87,700
8	4.0	1.0	7.0	8.5	6967	99,100
9	2.0	4.0	8.5	9.5	4710	67,000
10	3.0	3.0	11.0	12.0	5582	79,400
11	4.0	2.0	8.5	10.5	5301	75,400
12	4.0	2.0	9.0	9.5	6197	88,150

As shown in Table 1, the stiffness is higher when a greater proportion of the copolymer grease is used in place of the plasticizer. Cling, measured after 30 days aging, is also higher where a higher percentage of the copolymer grease and plasticizer blend is used. A stiffer film with higher cling is particularly advantageous for household film in that the film is less likely to tangle, tears easier from the roll, holds better to itself for sealing and gives a feeling of strength to the user. The copolymer grease/plasticizer blend mixes well and acts as an extrusion aid. It does not require operating conditions which significantly effect the degradation (color) of the vinylidene chloride copolymer resin.

It was also found that residual vinyl chloride and vinylidene chloride monomer levels were significantly lowered by use of the in-monomer addition of the grease copolymer without conventional plasticizer as compared with traditionally plasticized resins. The following Table II demonstrates the residual monomer data found. Control Run 1 was made with the traditionally plasticized vinylidene chloride copolymer resins, the other runs with the same vinylidene chloride copolymer resin only using the in-monomer addition of the grease copolymer as contemplated by the present invention in place of the plasticizer.



TABLE II
RESIDUAL MONOMER DATA (DRIED RESIN)

<u>Run No.</u>	<u>Residual Vinyl Chloride</u>	<u>Residual Vinylidene Chloride</u>
5	1-Control	0.1 ppm
	2	10.4 ppb
	3	58.0 ppb
	4	10.0 ppb
	5	<3 ppb
10	6	<3 ppb
	7	<3 ppb
		.47.0 ppm
		2.0 ppm
		*
		*
		*
		*

ppm = parts per million ppb = parts per billion

* No data available.

15 The grease copolymer used in the present invention is highly viscous and customarily of a sticky nature making it an inconvenient material to handle and clean from machinery components. Such processing and handling is greatly enhanced by the addition of a conventional plasticizer.

20 While certain representative embodiments and details have been shown for purpose of illustrating the invention, it will be apparent to those skilled in the art that various changes and applications can be made therein without departing from the spirit and scope of
 25 the invention.

CLAIMS

1. A high cling film comprising an extrudable resin composition comprising:
 - (a) a vinylidene chloride copolymer in which a major proportion of the copolymer is a vinylidene chloride monomer with a minor proportion of at least one other polymeric comonomer, and
 - (b) less than 10 percent by weight of total resin composition of a polymer blend comprising a grease copolymer having a peak molecular weight of from 500 to 7500 as determined by gel permeation chromatography and a non-polymeric ester plasticizer.

2. The film of Claim 1, wherein the vinylidene chloride copolymer comprises a major proportion of from 70 to 95 percent by weight of vinylidene chloride with the remainder comprising one or more ethylenically unsaturated comonomers.

3. The film of Claim 1 or 2 wherein the grease copolymer and plasticizer blend comprises from 3.0 to 7.0 percent by weight of the total film composition.



4. The film of Claim 1, 2 or 3 wherein the grease copolymer comprises an ethylene and vinyl acetate copolymer resin, and the proportion of vinyl acetate is from 10 to 55 weight percent of the grease copolymer and the peak molecular weight is within the range of from 1000 to 4000 as determined by gel permeation chromatography.

5. The film of any one of the preceding claims, wherein the grease copolymer has a melt flow rate in the range of from 5 to 50 dg/min at a temperature of 80°C when conducted in accordance with the procedure as herein defined.

6. The film of any one of the preceding claims, wherein the ratio of grease copolymer to plasticizer is in the range of from 4:1 to 1:4.

7. The film of any one of the preceding claims having a cling value in excess of 5 grams as measured by a 30-day cling test and a stiffness in excess of 5300 kg/cm² after 15 days aging as defined by a 2% Secant Modulus test.

8. The film of any one of the preceding claims, having a thickness of from 0.0051 mm to 0.076 mm.

9. The film of Claim 8, having a thickness of from 0.010 mm to 0.0254 mm.

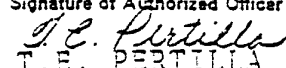
10. A method for preparing an extrudable vinylidene chloride copolymer composition having a high-cling and reduced vinylidene chloride and/or vinyl

chloride residuals, the process comprising the step of adding to the composition prior to polymerization a grease copolymer having a peak molecular weight within the range of from 500 to 7500 as determined by gel permeation chromatography, and a conventional plasticizer and polymerizing the copolymer composition with the in-monomer grease copolymer and plasticizer blend addition.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US81/01563

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				
INT. CL ³ CO8L ² 27/08; CO8L 91/00				
II. FIELDS SEARCHED				
Minimum Documentation Searched ⁴				
Classification System	Classification Symbols			
U.S.	260/23XA, 28.5AV, 31.8R, 31.8G; 525/5, 239			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶				
CHEMICAL ABSTRACTS: 1967 - TO DATE				
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴				
Category ⁸	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸		
A	US, A, 3,322,862, PUBLISHED 30 MAY 1967, SEE COL. 2, LINES 46-63; COL. 6, LINES 50-64 HAVENS ET AL.	1-10		
A	US, A, 4,209,437, PUBLISHED 24 JUNE 1980, COL. 3, LINES 12-31; TABLE I, FISHER	1-10		
A	US, A, 4,123,477, PUBLISHED 31 OCTOBER 1978 COL. 1, LINES 11-68; COL. 6, LINES 1-23 WATANABE ET AL..	1-10		
A	US, A, 3,713,965, PUBLISHED 30 JANUARY 1973 COL. 2, LINES 1-29; 50; EXAMPLE WIDIGER ET AL.	1-10		
A	US, A, 3,125,545, PUBLISHED 17 MARCH 1964 COL. 2, LINES 10-26; COL. 4, LINES 60-75 VAN CLEVE ET AL.	1-10		
A	GB, A, 917,083, PUBLISHED 30 JANUARY 1963 COL. 2, LINES 9-20. WHITELEY	1-10		
<p>¹⁵ Special categories of cited documents:</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </td> <td style="width: 50%; border: none;"> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or 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</p> </td> </tr> </table>			<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</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 on or after the priority date claimed</p> <p>"T" later document published on or 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</p>
<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</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 on or after the priority date claimed</p> <p>"T" later document published on or 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</p>			
IV. CERTIFICATION				
Date of the Actual Completion of the International Search ⁹	Date of Mailing of this International Search Report ¹⁰			
19 FEBRUARY 1982	02 MAR 1982			
International Searching Authority ¹¹	Signature of Authorized Officer ¹⁰			
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