

MULTILAYER POLYPROPYLENE FILM"

The present invention relates to a multilayer polypropylene film.

A biaxially stretched film of highly crystalline polypropylene is a packing material superior in transparency and stiffness, but it cannot be used, as it is, in automatic packing machines because of its poor heat sealing properties. In general, the heat sealing temperature of a stretched polypropylene film is higher than its stretching temperature so that film contraction takes place on heat sealing and the film returns to the unstretched state. As a result, film appearance becomes poor and sealing strength lowers.

In order to overcome these drawbacks, multilayer films are widely used which are produced by coating or laminating a resin having good heat sealing properties on a polypropylene film. Multilayer polypropylene films laminated with polyethylene or ethylene/vinyl acetate copolymer have

low heat sealing temperatures, but when they are used for packing rice crackers and the like for which a biaxially stretched polypropylene film is frequently used, they show a poor anti-scratching property, that is, they are easily scratched and lose their transparency. Further, they have a poor anti-blocking property, that is, they adhere to themselves so easily that pouches made of them are difficult to open. While propylene copolymers containing a small amount of comonomer such as ethylene or butene-1 are not scratched easily and have relatively good anti-blocking properties and are widely used, propylene/ethylene copolymers, which have frequently been used have the drawbacks that their heat sealing temperature is more than 20°C higher than that of polyethylene.

A low heat sealing temperature is clearly advantageous from an economical point of view because it increases the rate of making pouches of multilayer films. Consequently, the resins laminated on polypropylene film should have a low heat sealing temperature and good anti-scratching properties anti-blocking properties and transparency.

In order to lower the heat sealing temperature of propylene copolymers having good anti-scratching properties it is necessary (as is well known) to increase the comonomer content of the copolymers thereby to lower the crystallinity of the polymer, but propylene copolymers having an increased

comonomer content are difficult to produce on a commercial scale and their cost becomes high. Moreover, the slipperiness and anti-blocking property of multilayer films made of such copolymers tend to be poor due to the increase in the amount of amorphous polymer contained in them. Consequently, it has been difficult to use propylene copolymers in practice.

Propylene/ethylene copolymers containing a small amount of ethylene have so far been produced, but when the amount of ethylene copolymerized is increased to improve the heat sealing properties of the copolymers, large amounts of low-molecular amorphous polymers soluble in the polymerization medium are obtained as by-products. These amorphous polymers are so poor in commercial value that the by-production of them causes economical disadvantages such as a loss in monomers. Besides, they lower the flowability of the polymer slurry in solution in the polymerization solvent causing various problems in production such as a viscosity increase in the system and a reduction of the heat transfer coefficient of the polymerization reactor. When the flowability of the slurry is extremely poor, even withdrawing the produced polymer from the reactor becomes impossible using conventional techniques. Also in gas-phase polymerization, an increase in the amount of amorphous polymers makes the produced powdery polymer more adhesive and as a result the powdery polymer has poor flowability and adheres ^{the} of/polymerization reactor and

pipes, thereby making normal operation difficult. Further, the cold xylene-soluble portion of the copolymer increases and films made of the copolymer show a rapid reduction in slipperiness and anti-blocking properties. Attempts to overcome such reduction by adding large amounts of well-known lubricating agents and anti-blocking agents result only in a reduction in transparency or insufficient improvement of anti-blocking properties. Consequently, the copolymer cannot be used as a film.

Copolymerization of propylene, ethylene and α -olefin is disclosed in Japanese Patent Application (OPI) Nos. 35487/1974 (the term "OPI" as used herein refers to a "published unexamined Japanese patent application"), 79195/1976 and 16588/1977. These references, however, do not disclose a process for producing copolymers having satisfactory low-temperature heat sealing properties without the foregoing problems in an industrially advantageous manner, and the copolymers disclosed have a heat sealing temperature equal to or at best about 5°C lower than propylene/ethylene copolymers having an ethylene content of 4 to 5.5% by weight. Multilayer films produced by laminating copolymers prepared in accordance with these references, as a heat sealing layer, on biaxially stretched polypropylene film are well known. Japanese Patent Application (OPI) No. 11281/1977 discloses stretched composite films comprising a crystalline polypropylene layer and a crystalline propylene random copolymer layer containing 1 to

10% by weight of a straight chain α -olefin other than propylene and 0.1 to 4.0% by weight of ethylene. With these composite films a sufficient reduction in heat sealing temperature is not obtained and the heat sealing temperature is at best about 5°C lower than that of a stretched composite film having a propylene/ethylene copolymer layer containing 4.0% by weight of ethylene.

A propylene/butene-1 copolymer having good heat sealing properties is proposed in Japanese Patent Publication No. 19437/1966 wherein the propylene/butene-1 copolymer having a butene-1 content of 25 to 80% by weight is obtained in the presence of a mixture comprising a halide of a transition metal, an organoaluminum compound or its halide and an ester, amide or esteramide of phosphoric acid, and British Patent 1,452,424 proposes laminating propylene/ α -olefin random copolymer containing 5 to 20% by weight of a C_4 - C_{10} α -olefin. It has been found that because both these copolymers contain a large amount of polymer soluble in 20°C xylene (referred to as "cold xylene-soluble portion" herein), stretched composite films containing such copolymers alone are poor in slipperiness and anti-blocking properties, and when a large amount of a slipping agent is added to improve their properties the agent migrates to the surface of the films thereby markedly damaging their high transparency, which is a superior characteristic of biaxially stretched polypropylene film used as a base film of the composite films.

An object of the present invention is to obviate or alleviate the above-mentioned disadvantages experienced in the prior art.

According to the present invention, there is provided a
5 multilayer polypropylene film comprising a crystalline
polypropylene (as defined herein) layer and a crystalline
propylene/ α -olefin or crystalline propylene/ α -
olefin/ethylene copolymer layer containing 8 to 30% by
weight of at least one C₄ - C₁₈ α -olefin and, 0 to 5% by
10 weight of ethylene and also containing 10% by weight or
less of a 20°C xylene-soluble polymer.

In the accompanying drawings,

Figure 1 is a flow sheet illustrating one example of a
process for producing a copolymer for a multilayer
15 polypropylene film of the present invention, and

Figure 2 shows the relation between the content (weight
%) of the cold xylene-soluble portion in a crystalline
propylene/butene-1 copolymer and the blocking (g/100 cm²)
of a monolayer film made of the copolymer, the symbols O,
20 $\square$, $\bullet$ and Δ indicating the values for the copolymers
containing different contents of butene-1: 12 $\pm$ 0.5% by
weight for O, 15 $\pm$ 1% by weight for $\square$, 20 $\pm$ 1% by weight for
 $\bullet$ and 25 $\pm$ 1% by weight for Δ .

The crystalline polypropylene is preferably one which is
25 produced by conventional process and generally used as a
non-stretched film or stretched film itself or a base
film of a conventional multilayer polypropylene film. By
"crystalline polypropylene" is meant a crystalline
propylene homopolymer, a propylene random copolymer
30 having an ethylene content of up to 2% by weight or a
crystalline propylene-ethylene block copolymer having an
ethylene content of up to 12% by weight. The
crystallinity of the crystalline polypropylene is higher

than that of crystalline propylene copolymer. The crystalline propylene copolymer preferably contains 10 to 25% by weight of the α -olefin and preferably 0 to 3% by weight of ethylene. Preferably, the propylene copolymer has a cold xylene-soluble portion of 5% by weight or less. When the α -olefin content is less than 10% by weight, the heat sealing temperature cannot be lowered sufficiently. While when the α -olefin content is more than 30% by weight, the crystallinity of the copolymers becomes too poor. The content is more preferably 25% by weight or less.

The copolymer may or may not contain ethylene. It is necessary to limit the ethylene content to 5% by weight or less, preferably 3% by weight or less, because too large an ethylene content makes the anti-scratching properties poor.

The content of the cold xylene-soluble portion in the copolymers should be limited to 10% by weight or less. The reason for this will be shown with reference to the following example. The monolayer film (30 μ thick) of a propylene/butene-1 copolymer was prepared by blending the copolymer, 0.2% of di-tert-butyl p-cresol as a stabilizer, 0.5% of a silica type anti-blocking agent and 0.2% of a fatty acid amide (slipping agent) and passing the blend through a T-die extruder. Figure 2 shows the relation between the blocking properties and butene-1 content (and the content of cold xylene-soluble portion) of the film. It is apparent from Fig. 2 that the blocking properties are somewhat affected by the butene-1 content, but that they are largely affected by the content of cold xylene-soluble portion.

When the amount of an anti-blocking agent added to the copolymer rich in the cold xylene-soluble portion is increased, transparency is extremely reduced so that the copolymer is not suitable as a packing film. Further, when the cold xylene-soluble portion is above a certain level, desirable anti-blocking properties cannot be obtained if a well known type of anti-blocking agent is added in large amounts. Slipperiness is largely affected, like the blocking properties by the cold xylene-soluble portion.

High quality packing films therefore cannot be obtained by a mere increase in the comonomer content of copolymer layer, and a decrease in the content of cold xylene-soluble portion is further required for the copolymer.

The multilayer polypropylene film of the present invention can be obtained by laminating the crystalline propylene/ α -olefin or crystalline propylene/ α -olefin/ethylene copolymer on one side or both sides of the crystalline polypropylene film. For example, the multilayer film can be obtained as follows: (1) a method comprising placing a film made of the copolymer on the base film, with an adhesive between them, and passing them through a pressure roll; (2) a method comprising coating a copolymer solution or dispersion in a solvent (e.g. toluene) on the base film; (3) a method comprising extrusion-coating the copolymer on the base film; and (4) a method comprising extruding the copolymer and base copolymer through separate extruders and laminating them into a film, while molten, in the same die or at the outlet thereof.

The multilayer film of the present invention, at least the polypropylene layer of the film, is preferably stretched uniaxially or biaxially. This stretched multilayer polypropylene film is produced in a conventional manner. The crystalline propylene/ α -olefin or crystalline propylene/ α -olefin/ethylene copolymer is laminated on the crystalline polypropylene sheet, a base sheet, followed by stretching. This lamination is carried out as follows:

- (1) Co-extrusion, i.e., a method comprising laminating both polymers into a film, while molten, in a sheet-forming die or at the outlet thereof.
- (2) A method comprising forming both polymers into solid sheets, followed by laminating.
- (3) A method comprising stretching the polypropylene base sheet uniaxially, while hot, in the direction of extrusion through a group of metallic rolls, and then laminating the molten or solid propylene copolymer sheet on the base sheet.

The crystalline propylene/ α -olefin or crystalline propylene/ α -olefin/ethylene copolymer used in the multilayer polypropylene film according to the present invention is preferably produced by copolymerizing propylene, an α -olefin having 4 to 18 carbon atoms and 0 to 5% by weight of ethylene in the presence of a catalyst system comprising (i) titanium trichloride produced by a method comprising reducing titanium tetrachloride with an organo-aluminum compound, and reacting the reduced product with a complexing agent, e.g. an ether, and a halogen compound, and (ii) an organo-aluminum compound. Examples of such a production process are described and claimed in our copending British Patent Application No. 7920608 (2027720A) from which the present Application is divided.

Referring now to Fig. 1 of the drawings, to produce the copolymer, a polymerization reactor is supplied with liquid propylene through line 2, α -olefin having 4 to 18 carbon atoms (e.g., butene-1) through line 3, a molecular weight regulating agent (e.g., hydrogen) through line 4 and a catalyst through line 5.

Polymerization is carried out under a pressure sufficient to maintain the monomer mixture in a liquid state. The produced polymer slurry is withdrawn batchwise, preferably continuously, from reactor 1 through valve 6 and introduced into an upper part 8 of a counter-current washing tower 7 (referred to as "top feed" hereinafter). To the lower portion of the tower 7 is supplied a liquid propylene (preferably fresh propylene) containing no slurry-soluble polymer (mainly amorphous polymer) or a liquid monomer mixture (referred to as "bottom feed" hereinafter) via line 9. In supplying the liquid monomer mixture to the bottom of the tower, the mixing ratio of the monomers can be properly selected independently of the mixture supplied to the reactor, taking into account the properties of the copolymer and the features of the process.

An alcohol or a mixture of an alcohol and an epoxide is supplied, directly or after dilution with liquid propylene or a liquid monomer mixture through line 9, 16 or 17. In order to bring the polymer into intimate contact with the alcohol or the mixture thereby enhancing the washing effect, supplying the alcohol or the mixture through line 17 is most desirable.

Slurry-soluble polymers and reaction products between the residual catalyst in the polymer slurry and the alcohol are withdrawn through an overflow line 10 and introduced into recovery equipment for amorphous polymers. In the washing tower 7, the polymer slurry is brought into counter-current contact with liquid propylene or liquid monomer mixture of the bottom feed, and the slurry-insoluble polymer is withdrawn from the bottom through a line 11 and introduced into a flash tank 13, with ^{the} pressure applied thereto being reduced to nearly atmospheric pressure by the action of a valve 12 which is interlocked with a level (or concentration) controller (LC) for the deposited slurry at the bottom.

The monomers volatile under atmospheric pressure are vaporized in the flash tank 13 and sent to a purification stage through line 14. The polymer separated in the flash tank 13 is sent directly or, if necessary, via after-treatments such as catalyst decomposition, to a hopper or granulator through a valve 15.

The function of the counter-current washing tower is firstly to separate liquid monomer mixture from the top feed and withdraw it together with the bottom feed ascending from the lower part through the overflow line at the top of the tower, and secondly to wash the slurry-insoluble polymer in the top feed with the bottom feed and to discharge it together with a part of the bottom feed from the bottom of the tower.

As the structure of the counter-current washing tower, the tower shown in Japanese Patent Application (OPI) No. 79589/1975 is preferably used since it satisfies the aforesaid requirements.

The present invention will be illustrated more clearly with reference to the following examples and reference examples, which are not, however, to be interpreted as limiting.

The film properties reported in the examples were measured as follows:

(1) Cold xylene-soluble portion

5 g of the polymer was dissolved in 500 ml of boiling xylene, and the solution was gradually cooled to room temperature and allowed to stand at 20°C for 4 hours. After filtering the deposited polymer, xylene was evaporated from the filtrate and the residue was dried at 60°C under reduced pressure to recover a cold xylene-soluble polymer. The content of the cold xylene-soluble polymer was expressed as a percentage of the polymer sample.

(2) Heat sealing temperature

Using a heat sealer, a test sample (25 mm in width) was prepared by pressing a layer of pieces of the same film under a weight of 2 kg/cm² at a given temperature for 2 seconds. A peeling test was carried out under a peeling rate of 200 mm/min and a peeling angle of 180° and the temperature at which peeling resistance was 300 g/25 mm was taken as the heat sealing temperature.

(3) Transparency (haze)

A test was carried out in accordance with ASTM D 1003.

(4) Blocking

A blocked sample was prepared at 60°C for 3 hours under a weight of 40 g/cm², and measured by blocking on a blocking tester (produced by Shimadzu Seisakusho Co.).

(5) Anti-scratching property

A laminated film test sample was placed with its laminated side turned up on the bottom of a polymethyl methacrylate box (13 cm x 11 cm x 5 cm (deep)), and 100 cc of 15 to 25-mesh sea sand was placed thereon. The box was fixed to a vibrator and vibrated horizontally for 15 seconds at a rate of 300 times/min. After vibration, the laminated film was washed with water, dried and tested for haze according to ASTM D 1003. The difference in haze before and after the anti-scratching test was taken as the measure of the anti-scratching property.

Examples of the preparation of the propylene/ α -olefin and propylene/ α -olefin/ethylene copolymers will now be described.

PREPARATION EXAMPLE 1

1. Preparation of Catalyst

(1) Preparation I

After replacing the atmosphere in a 200-liter reactor with argon, dry hexane (40 liters) and titanium tetrachloride (10 liters) were added thereto and the mixed solution was kept

at -5°C. A solution comprising dry hexane (30 liters) and ethylaluminum sesquichloride (23.2 liters) was added dropwise thereto so that the reaction system was kept at -3°C or less. Thereafter, stirring was continued at this temperature for 2 hours. After the reaction was finished, the reaction system was allowed to stand, and the reduction product was separated at 0°C from the liquid portion and washed twice with hexane (40 liters). Thus, 16 kg of the reduction product was obtained.

(2) Preparation II

The reduction product obtained in Preparation I was slurried in n-decalin, and the slurry concentration was adjusted to 0.2 g/cc, followed by heat treatment at 140°C for 2 hours. After the reaction was finished, the supernatant liquid was discharged and the product was washed twice with hexane (40 liters) to obtain a titanium trichloride composition (A).

(3) Preparation III

11 kg of the titanium trichloride composition (A) prepared in Preparation II was slurried in toluene (55 liters), and iodine and diisoamyl ether were added thereto so that the molar ratio of titanium trichloride composition (A) to I₂ to diisoamyl ether was 1:0.1:1.0. The reaction was carried out at 80°C for 1 hour to obtain a titanium trichloride solid catalyst (B).

2. Pre-Treatment of Catalyst System

After the atmosphere in a 5-liter reactor equipped with a stirrer was replaced with argon, dry n-heptane (1 liter),

the foregoing titanium trichloride solid catalyst (B) (16 g) and diethylaluminum chloride (70 g) were added thereto. After the atmosphere in the reactor was replaced with propylene, the contents were heated to 50°C and reaction was carried out with the addition of propylene (300 g) while stirring. A catalyst system (C) was thus obtained.

3. Propylene/ α -Olefin Copolymerization

The atmosphere in a 200-liter polymerization reactor equipped with a stirrer was sufficiently replaced with propylene, and technical-grade heptane (68 liters) was added thereto. The whole catalyst system (C) was added and washed into the reactor with technical-grade heptane so that the total amount of the heptane in the reactor was 70 liters. Thereafter, propylene (6.5 kg) and butene-1 (7 kg) were added, and the contents of the reactor were raised to 50°C, when gauge pressure was 4 kg/cm². While strictly regulating the composition of butene-1/propylene in the gaseous phase under a proper hydrogen partial pressure, butene-1 (7.0 kg) and propylene (22.5 kg) were continuously supplied.

After polymerization, the catalyst in the copolymer slurry was removed by decomposition with isobutanol, and the polymer was then purified to obtain 31 kg of a powdery copolymer. The properties of the copolymer were as follows:

Intrinsic viscosity (135°C, in tetralin	- 1.49
Butene-1 content (IR spectrum)	- 16.6 mol %
Yield of powdery copolymer	- 84.5 wt %
Bulk density	- 0.43
Cold xylene-soluble portion content	- 8.5 wt %
Melt index	- 11.0 g/10 min
Stiffness (Young's modulus)	- 4500 Kg/cm ²
Transparency (haze)	- 5.7 %
Blocking	- 32 g/100 cm ²

PREPARATION EXAMPLE 2

The atmosphere in a 200-liter polymerization reactor equipped with a stirrer was replaced with propylene, and liquid propylene (32.3 kg) and liquid butene-1 (19.1 kg) were added thereto. Thereafter, diethylaluminum chloride (50 g), the titanium trichloride solid catalyst (B) prepared in Preparation Example 1 (4 g) and methyl methacrylate (8g) were added to the reactor and the contents of the reactor were heated to 60°C.

During polymerization, propylene was added so that the butene-1 concentration of the liquid phase was constant. The total amount of propylene added was 13 kg.

After 4 hours' polymerization, the polymer slurry was poured into a mixture of isobutanol and n-heptane (60°C) and treated for 30 minutes. The solvent containing amorphous polymers was then separated from the slurry.

After drying, 23.3 kg of a powdery polymer was obtained, and 0.8 kg of amorphous polymer was obtained from the separated solvent. The butene-1 content of the powdery polymer was 15.2% by weight. The bulk density and content of cold xylene-soluble portion of the copolymer and the characteristics of a film thereof (30 μ thick, produced by a T-die extruder) are shown in Table 1.

PREPARATION EXAMPLE 3

Copolymerization was carried out in the same manner as in Preparation Example 2 except that the butene-1 content of the copolymer was changed to 20.5% by weight. The results are shown in Table 1.

PREPARATION EXAMPLE 4

Copolymerization was carried out in the same manner as in Preparation Example 2 except that the butene-1 and ethylene contents of the copolymer were changed to 10% by weight and 3% by weight, respectively. The results are shown in Table 1.

TABLE 1

Examples	Composition of Copolymer (wt%)			Bulk Density	Cold Xylene- Soluble Portion (wt%)	Melt Index (g/10 min)	Heat Sealing Temper- ature (°C)	Stiffness (Young's modulus) (kg/cm ²)	Transpar- ency (haze) (%)	Blocking (g/100 cm ²)
	Propylene	Butene-1	Ethylene							
2	84.8	15.2	---	0.51	3.5	6.5	111	5,100	2.7	48
3	79.5	20.5	---	0.44	7.3	7.3	102	4,600	2.4	55
4	87.1	9.7	3.2	0.50	5.1	7.0	110	4,200	2.9	56

PREPARATION EXAMPLE 5

Liquid propylene (900 kg/hr), liquid butene-1 (650 kg/hr), the solid catalyst (B) prepared in/^{Preparation}Example 1 (50 g/hr), diethylaluminum chloride (600 g/hr) and methyl methacrylate (60 g/hr) were continuously supplied to a 30 cubic meter polymerization reactor in the presence of hydrogen, and propylene was polymerized at 60°C according to the flow method. During that time, the pressure in the reactor was 18 to 18.8 kg/cm²G, and the produced polymer slurry was withdrawn from the bottom of the reactor so that the level in the reactor was kept constant.

The polymer slurry withdrawn under this condition comprised a propylene/butene-1 solid copolymer (450 kg/hr), a so-called atactic polymer (12 kg/hr) by-product soluble in liquid propylene, and unreacted liquid propylene and butene-1 (1,100 kg/hr) containing most of the aluminum compound supplied. This polymer slurry was continuously withdrawn from the bottom of the reactor and supplied to the top 8 of a counter-current multi-stage washing tower 7 (Figure 1).

Isobutanol (370 g/hr), a deactivator, was supplied under pressure to the middle part 17 of the washing tower.

On the other hand, purified liquid propylene (50 to 52°C) was continuously supplied at a rate of 1,100 kg/hr to the bottom 9 of the tower. Agitation in the tower was carried out at a very slow rate of 12 rpm. During that time, the

pressure in the tower was 14.1 to 15.0 kg/cm²G. The polymer which deposited at the bottom of the reactor was continuously sent to a flash tank 13 through a reducing valve 12 interlocked with a level controller LC and a line 11.

From the top 10 of the tower was withdrawn liquid propylene and butene-1 (1,500 kg/hr) containing the aluminum component of the catalyst and the atactic polymer (12 kg/hr), and it was introduced into an atactic polymer recovery unit. Loss of fine powdery polymer contained therein was 1% or less. The slurry withdrawn from the bottom of the tower was separated in a flash tank 13, and a beautiful powdery copolymer was obtained from the bottom of the tank.

The produced powdery copolymer was tested for polymer characteristics such as butene-1 content, content of cold xylene-soluble portion and residual ash, and film characteristics such as film blocking (the film was 30 μ thick and produced by extruding a blend of the copolymer and a common additive through a 40 mm ϕ T-die). These characteristics are shown in Table 2 together with the results of the below-described Preparation Examples.

The specifications of the counter-current washing tower used in this Preparation Example were as follows:

Diameter of tower	:	600 mm ϕ
Height of tower	:	8,200 mm
Rotating axis	:	Has 10 conical plates

5 The copolymer after washing had excellent properties as is apparent from the following: Ash content was very small, total ash: 60 ppm, TiO_2 : 34 ppm, Al_2O_3 : 15 ppm; content of cold xylene-soluble portion: 3.5% by weight; film characteristics--blocking: 34 g/cm², haze: 2.5%, heat sealing temperature: 109°C, fish eyes were not present

PREPARATION EXAMPLE 6

10 Copolymerization was carried out in the same manner as in Example 5 except that the feed rates of liquid propylene and liquid butene-1 were 1,200 kg/hr and 400 kg/hr, respectively. The results are shown in Table 2 together with the film characteristics.

T A B L E 2

Characteristics and Copolymer Film Characteristics

Catalyst	Example 5 Solid Catalyst (B)	Example 6 Solid Catalyst (B)
Feed rate of titanium component (g/hr)	50	50
Feed rate of aluminum component (g/hr)	600	600
Polymerization Results		
Powdery copolymer (kg/hr)	450	550
Atactic polymer (kg/hr)	3	3
Catalytic efficiency (g/g)	9,000	11,000
Polymer Characteristics		
Total ash (ppm)	60	55
TiO ₂ (ppm)	34	32
Al ₂ O ₃ (ppm)	15	12
Color of pellet	Good	Good
General Properties and Film Characteristics		
Butene-1 content (weight%)	15.5	8.0
Ethylene content (weight%)	0	0
Content of cold xylene-soluble portion (%)	1.8	2.4
Melt index (g/10 min)	10.5	11.0
Haze (%)	2.5	2.8
Heat sealing temperature (°C)	109	122
Blocking (g/100 cm ²)	34	21
Young's modulus (kg/cm ²)	4,900	6,700

PREPARATION EXAMPLE 7

Copolymerization was carried out in the same manner as in Example 5 except that the feed rates of liquid propylene, liquid butene-1 and ethylene were 1,300 kg/hr, 450 kg/hr and 40 kg/hr, respectively. The characteristics of the resulting copolymer are shown in Table 3.

PREPARATION EXAMPLE 8

Copolymerization was carried out in the same manner as in Example 5 except that the feed rates of liquid propylene, liquid butene-1 and hexene-1 were 1,200 kg/hr, 450 kg/hr and 50 kg/hr, respectively. The characteristics of the resulting copolymer are shown in Table 3.

PREPARATION EXAMPLE 9

Copolymerization was carried out in the same manner as in Example 5 except that the feed rates of liquid propylene and liquid butene-1 were 700 kg/hr and 800 kg/hr, respectively. The characteristics of the resulting copolymer are shown in Table 3.

T A B L E 3
Characteristics and Copolymer Film Characteristics

	<u>Example 7</u>	<u>Example 8</u>	<u>Example 9</u>
Comonomer content (weight%)			
Butene-1	18.0	8.2	22.8
Ethylene	2.7		
Hexene-1		2.2	
Cold xylene-soluble portion (%)	4.5	2.1	4.6
Melt index (g/10 min)	10.5	7.5	8.0
Haze (%)	2.7	2.9	1.5
Heat sealing temperature (°C)	118	120	101
Blocking (g/100 cm ²)	38	20	40
Young's modulus (kg/cm ²)	6,200	6,400	3,100

Examples of multilayer polypropylene films according to the invention and Comparative Examples will now be described.

EXAMPLE 1

Isotactic polypropylene sheet (melt index, 2.0) was stretched to five times as long as its original length in the lengthwise direction to obtain uniaxially stretched sheet of 18 μ in thickness. The propylene/butene-1 copolymer shown in Table 4 was extruded into a sheet of 60 μ thick from a T-die extruder and laminated on one side of the stretched sheet.

The two-layer laminated sheet thus-obtained was stretched in the widthwise direction so that stretching ratio was 6, and heat-treated under tension at 150°C for 5 seconds to obtain a two-layer laminated film. The characteristics of this two-layer film are shown in Table 4.

EXAMPLES 2 AND

COMPARATIVE EXAMPLES 1 AND 2

Laminated film was produced in the same manner as in Example 1 except that the propylene copolymers shown in Table 4 were each laminated on the uniaxially stretched polypropylene sheet. The characteristics of the two-layer laminated films are shown in Table 4.

EXAMPLE 3

The same isotactic polypropylene and propylene/butene-1 copolymer as used in Example 1 were extruded through separate extruders and laminated into a two-layer sheet by the co-extrusion technique using a die having two manifolds and one land. The laminated sheet was then subjected to five-fold

lengthwise stretching and then six-fold widthwise stretching to obtain a two-layer film comprising a polypropylene layer of 30 μ thick and propylene/butene-1 copolymer layer of 10 μ thick. The characteristics of this two-layer film are shown in Table 5.

Attention is drawn to our copending British Patent Application No. 7920608 (2027720A) from which the present Application is divided.

TABLE 4

	Propylene Copolymer			Characteristics of Multilayer Film			
	Butene-1 Content (wt%)	Ethylene Content (wt%)	Content of Cold Xylene- Soluble Portion (wt%)	Haze (%)	Heat Sealing Temperature (°C)	Blocking (g/100 cm ²)	Anti- Scratching Property (%)
Examples							
1	15.2	0	3.5	2.1	111	21	5.1
2	20.5	0	7.3	1.9	101	42	6.3
3	15.2	0	3.5	1.8	109	23	5.3
Comparative Examples							
1	19.8	0	17.7	4.9	124	120 or more.	4.5
2	0	7.0	14.8	4.2	118	103	12.4



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CLAIMS

1. A multilayer polypropylene film comprising a crystalline polypropylene (as defined herein) layer and a crystalline propylene/ α -olefin or crystalline
5 propylene/ α -olefin/ethylene copolymer layer containing 8 to 30% weight of at least one C_4 - C_{18} α -olefin and 0 to 5% by weight of ethylene and also containing 10% by weight or less of a 20°C xylene-soluble polymer.
2. The multilayer polypropylene film of claim 1, wherein
10 said α -olefin is butene-1.
3. The multilayer polypropylene film of claim 1 or 2, wherein the content of α -olefin is 10 to 25% by weight.
4. The multilayer polypropylene film of claim 1, wherein the content of ethylene is 0 to 3% by weight.
- 15 5. The multilayer polypropylene film of claim 1, 2, 3 or 4, wherein the content of the 20°C xylene soluble polymer is 5% by weight or less.
6. A multilayer polypropylene film as claimed in claim 1, substantially as hereinbefore described with reference to
20 any one of Examples 1 to 3.

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