CONVENTION

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

We, EASTMAN CHEMICAL COMPANY of 100 North Eastman Road, Kingsport, Tennessee 37660, United States of America state the following in connection with Australian Application No. 79687/94:

1. We are the nominated person.

2. The nominated person is the assignee of the actual inventors.

3. The nominated person is the assignee of the applicants of the basic application listed in the declaration under Article 8 of the PCT.

4. The basic application is the application first made in a Convention country in respect of the invention.

Dated: 13 March 1996

By PHILLIPS ORMONDE & FITZPATRICK
Patent Attorneys for the Applicant
By:  

To: The Commissioner of Patents

PHILLIPS ORMONDE & FITZPATRICK
367 Collins Street
Melbourne, Australia, 3000

Ref: 392300

1925x
1. A non-oriented layered film comprising
   (a) a first amorphous crystallisable polyester layer consisting essentially of polyethylene terephthalate having a melting point greater than about 238°C. and a heat of fusion of greater than about 9 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20°C/min, and
   (b) a second amorphous, heat-sealing polyester layer consisting essentially of repeat units from terephthalic acid, about 85-93 mol % ethylene glycol and about 15-7 mol % cyclohexanediol, said second polyester having a heat of fusion of greater than about 0.5 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20°C/min. the total thickness of said second polyester layer being less than about 50% of the total thickness of said film.

10. A non-oriented polyester film consisting essentially of an amorphous, heat-sealing polyester wherein said heat-sealing polyester consists essentially of repeat units from terephthalic acid, about 85-93 mol % ethylene glycol and about
15.7 mol % cyclohexanediol wherein said heat-sealing polyester has a heat of fusion of greater than about 0.5 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20°C./min.
Monolayer and multilayer polyester film which comprises at least one layer of a heat-sealing polyester which is crystallizable to the extent of allowing mixtures thereof to be made with other crystallizable polyesters for crystallization without sticking is disclosed. The heat-sealing polyester is polyethylene terephthalate modified with about 7-15 ml. % cyclohexanedimethanol. In multilayered films, another layer of readily crystallizable polyethylene terephthalate is used.
Technical Field

The present invention relates to polyester film, both monolayer and multilayer. The film comprises at least one layer of a heat-sealing polyester which is crystallizable to the extent of allowing mixtures thereof to be made with other crystallizable polyesters for crystallization without sticking. The heat-sealing polyester is polyethylene terephthalate modified with about 7-15 mol % cyclohexanedimethanol. In multilayered films, another layer of readily crystallizable polyethylene terephthalate (PET) is used.

Background of the Invention

It is known in the art that amorphous polyesters can be extruded with crystallizable polyesters to improve performance of the film. Performance improvements over monolayer crystallizable polyester films include high temperature sealing, solvent sealing, and lower cutting force during trimming. Crystallizable polyesters used as a heat-sealing layer often results in poor performance. Amorphous polyester resins cause problems when being handled as waste material (hereinafter sometimes called "regrind") which is generated during processing. When mixed with crystalline polyester pellets and dried at a temperature above the glass transition temperature of the amorphous polyester, the regrind softens and sticks together, forming large clumps. These clumps make drying of the regrind very difficult and cause significant problems with air flow in a dryer and also when feeding to an extruder.

Some techniques for overcoming this sticking problem include melting the regrind with crystallizable
polyesters using devices specially equipped for this process and then reforming the extrudate into pellets that can later be thermally crystallized. Although this technique may alleviate the sticking problems, the cost can be relatively expensive.

This invention provides a polyester composition which offers advantages due to its heat-sealability, while at the same time crystallize to sufficient levels to allow mixing and drying with crystallizable polyesters.

Polyesters containing repeat units from terephthalic acid, ethylene glycol and cyclohexanediol are known in the art. For example, see U. S. Patent Nos. 4,373,002; 4,091,150; 4,405,400; 4,011,358; 4,765,999; 4,399,179; 4,946,743; 4,375,494 and 2,901,466. Some of the films disclosed in these patents are oriented. In others, the heat-sealing layer is not as described and claimed herein. For example, U. S. Patent No. 4,765,999 discloses a dual layered film wherein the heat-sealing layer is a polyester having repeat units from terephthalic acid, ethylene glycol and 1,4-cyclohexanediol. This heat-sealing polyester contains a greater number of repeat units from 1,4-cyclohexanediol than claimed herein, making the heat-sealing layer too difficult to crystallize and thus, would result in sticking when mixed with other polyesters during crystallization.

Japanese Patent 62,222,845 discloses a laminated heat-sealable polyester film comprised of (1) a crystallizable PET containing up to 10 mol % of comonomer that has a heat of fusion of at least 7 cal/g and (2) a PET copolymer containing 10-20 mol % isophthalic acid that has a heat of fusion of up to 5 cal/g. The film is oriented and used for pouches for boiling food for sterilization. An important feature of
between the layers is the refraction index. A preferred range is disclosed for optimum properties. This patent does not address regrind nor the crystallizability of the second layer. Furthermore, it does not mention the use of PET copolymers containing 1,4-cyclohexane dimethanol.

Japanese Patent 60,253,545 discloses a laminated polyester film for shrink-packaging comprised of (1) a copolyester modified with 5 to 50 mol % 1,4-cyclohexane dimethanol and (2) PET. The total thickness of the copolyester layer is 20-70% of the entire structure. An important property of the film is shrinkage. Again, this patent does not address regrind nor the crystallisability of the copolyester layer.

Description of the Invention

According to one embodiment of this invention, there is provided a non-oriented film of an amorphous, heat-sealing, slowly crystallisable polyester consisting essentially of repeat units from terephthalic acid, about 85-93 mol % ethylene glycol and about 15-7 mol % cyclohexanediethanol.

According to another embodiment of the invention, there is provided a non-oriented film comprising

(a) a first amorphous crystallisable polyester layer consisting essentially of polyethylene terephthalate having a melting point greater than about 238°C., a heat of fusion of greater than about 9 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20° C./min, an I.V. of about 0.50 dL/g to about 1.00 dL/g, and

(b) a second amorphous, heat-sealing polyester layer having an I.V. of about 0.50 dL/g to about 0.90 dL/g and wherein said heat-sealing polyester consists essentially of repeat units from terephthalic acid, about 85-93 mol % ethylene glycol and about 15-7 mol % cyclohexanediethanol, said heat-sealing polyester having a heat of fusion of greater than about 0.5 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20° C./min, the total thickness of said second heat-sealing polyester layer being less than about 50% of the total thickness of said film.
terephthalate having a melting point greater than about 238°C, a melt heat of fusion of greater than about 9 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20°C/min, an I.V. of about 0.50 dL/g to about 1.00 dL/g, and

b) an amorphous, heat-sealing layer of slowly crystallizable polyester having an I.V. of about 0.50 dL/g to about 0.90 dL/g and consisting essentially of repeat units from terephthalic acid, about 85-93 mol % ethylene glycol and about 15-7 mol % cyclohexanedimethanol, the total thickness of slowly crystallizable polyester being less than about 50% of the total thickness of said film.

The monolayer film described above is useful in that it is readily heat-sealable to various substrates such as paper, paperboard, plastic, metal and wood, but at the same time is slowly crystallizable such that it can be reground or chopped into particles and crystallized with virgin material to an extent that sticking of particles is not a problem. It is useful as packaging material, such as in fabricated boxes, food trays and blister packaging. The film may be used as such or may be molded, thermoformed, or the like to make articles such as trays. Also, it may be extruded or coextruded directly into mold cavities. It has been discovered that the properties of heat-sealability and crystallizing ability can be carefully balanced by providing a polyester consisting essentially of repeat units from terephthalic acid, about 85-93 mol % ethylene glycol and about 15-7 mol % cyclohexanedimethanol. Below about 7 mol % cyclohexanedimethanol, the polyester becomes too readily crystallizable, and heat-sealability is adversely affected. Above about 15 mol %
cyclohexanediol, the polyester becomes too difficult to crystallize, and has a tendency to stick when crystallization with other polyester particles is attempted. For example, polyethylene terephthalate modified with 3.5 mol % 1,4-cyclohexanediol is too readily crystallizable and heat-sealability is poor. On the other hand, polyethylene terephthalate modified with about 30 mol % 1,4-cyclohexanediol is so difficult to crystallize, sticking problems are encountered when crystallization with other polyesters is attempted.

For the purposes of this invention, the term "readily crystallizable" is preferably defined as when the crystallization half-time from the glassy state is in the range of 2 minutes, more preferably 1 minute, or less.

The term "slowly crystallizable" is preferably defined as when the crystallization half-time from the glassy state is in the range of 2 minutes or greater, preferably 3 minutes or greater.

The technique for following the rate of crystallization consists primarily in following the increase in depolarization of plane-polarized light by the polyester. The method used in this invention is primarily that shown in "A New Method for Following Rapid Rates of Crystallization", I. Poly (hexamethylene adipamide), J. H. Magill, Polymer, Vol. 2, page 221-233 (1961) with the exception that Magill uses a polarizing microscope as the source of light and light-collection lenses. In measuring the crystallization half-times of the present invention, a helium-neon laser [with a small angle light scattering technique (SALS)] was used as was shown by Adams and Stein in J. Polymer Sci. A2, Vol. 6 (1962).

Crystallization from the "glass or glassy state" is a term well-known in the art. For instance, it is
by R. S. Stern and A. Misra.

Crystallization half-times are measured at the time in which the transmitted intensity is half of the maximum intensity achieved.

The method used is generally as follows:

1. Melt the sample to remove existing crystallinity;
2. Bring the temperature of the sample polyester to a temperature below the glass transition temperature (crystallization from the glass or glassy state);
3. Crystallize the sample polyester at a predetermined temperature;
4. Record the transmitted light intensity plotted versus time;
5. Find the time at which the transmitted intensity is half of the maximum intensity achieved.

In multilayered structures, the layer which is essentially polyethylene terephthalate provides strength, support, and potentially lower cost to the film. By "essentially polyethylene terephthalate", it is meant polyethylene terephthalate homopolymer or a copolymer having up to a total of about 10 mol % repeat units from one or more other conventional dicarboxylic acids, glycols, or combinations thereof. Included as examples of the more conventional acids are terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, cyclohexanedicarboxylic acid and the like or their alkyl esters. Included as examples of the more conventional glycols are diethylene glycol, butanediol, hexanediol, neopentyl glycol, etc.

The cyclohexanedicarboxylic acid may be 1,4- or 1,3-isomers and may be cis, trans, or a mixture thereof.
The polyesters may be mixtures of polyesters achieving the aforementioned level of cyclohexanedicarboxylate.

The readily crystallizable polyester and the heat-sealing polyester are produced by esterification and polycondensation techniques well known in the art. By the term "polyester", we intend to include copolyester.

The "crystallizable polyester", as defined by this invention, is further characterized by having a melting point greater than about 238°C and a melt heat of fusion of greater than about 9 cal/g as measured by a differential scanning calorimeter, using a scan rate of about 20°C/min. The monolayer film may be produced by conventional extrusion or casting techniques. The multilayered films may be produced by conventional coextrusion, lamination, or the like. The readily crystallizable layer may have a layer of the heat-sealable layer applied to one or both sides. The film may be of any convenient thickness, but total thickness will normally be between about 5 and about 50 mil.

Normally, the heat-sealing polyester in multilayered films will account for about 5–50% of the total thickness of the film.

Examples

The following examples are submitted for a better understanding of the invention.

In the examples, "Polyester A" is polyethylene terephthalate modified with about 1.5 mol % 1,4-cyclohexanedicarboxylate, a readily crystallizable copolyester having an I.V. of about 0.76 dL/g. "Polyester B" is a copolyester having repeat units from terephthalic acid, about 90 mol % ethylene glycol and about 10 mol % 1,4-cyclohexanedicarboxylate, a slowly crystallizable copolyester having good heat sealability and an I.V. of about 0.68 dL/g. "Polyester C" is a crystallizable
polyester having an I.V. of about 0.76 dL/g, and having repeat units from
terephthalic acid, 96.5 mol % ethylene glycol and 3.5 mol % 1,4-
cyclohexanedicarboxylic acid. "Polyester D" is essentially non-crystallisable, has an
I.V. of 0.75 dL/g and has repeat units from terephthalic acid, about 70 mol %
ethylene glycol and about 30 mol % 1,4-cyclohexanedicarboxylic acid.

The first 11 examples were prepared with a 3.5" Wexlex (main) extruder and
a 1.5" Davis Standard (satellite) extruder in conjunction with a 3 layer Dow feed
block.

Example 1 - A 10 mil film was extruded from Polyester A. One mil (0.001")
of Polyester B was coextruded on each side of the 10 mil structure.

A control sample was also prepared by coextruding 1 mil of Polyester C on
each side of the 10 mil film.

The film structures were then evaluated for high temperature heat sealing
properties. The test consisted of sealing films to themselves using a heated bar
375°F for 2 seconds with 60 psi bar pressure. Samples were cut to produce a one inch by 4 inch test specimen. Bond strengths were determined using an Instron tensile testing machine to pull the bonded specimens at a 180° angle. The results, measured in grams/mm, unexpectedly indicated about a 30% improvement in peel strength with samples made from the coextruded modified polyester compared to the control (125.3 g/mm versus 96.1 g/mm).

Example 2 – An 8-mil film was extruded from Polyester A. Two mils (0.002") of Polyester B, as described in Example 1, were coextruded on each side of the 8-mil structure.

A control sample was also prepared by coextruding 2 mils of Polyester C on each side of the 8-mil film.

The films were heat sealed and tested as described in Example 1. The coextruded modified copolyester, unexpectedly, had about a 50% higher peel strength as compared to the control sample (207.6 g/mm versus 137.3 g/mm).

Example 3 – A 6-mil film was extruded from Polyester A. Three mils (0.003") of Polyester B, as described in Example 1, were coextruded on each side of the 6-mil structure.

A control sample was also prepared by coextruding 3 mils of Polyester C on each side of the 6-mil film.

The films were heat sealed and tested as described in Example 1. The coextruded modified copolyester, surprisingly, had about a 290% higher peel strength as compared to the control sample (193.4 g/mm versus 49.5 g/mm). This significant increase in peel strength was totally unexpected.

Example 4 – Films were coextruded as described in Example 1. A control sample was also prepared as described in Example 1.
The film structures were then evaluated for high temperature heat sealing properties. The test consisted of sealing the films to 10 mil substrates made from Polyester D using a heated bar at 375°F for 2 seconds with 60 psi bar pressure. Samples were cut to produce a one-inch by 4-inch test specimen. Bond strengths were determined using an Instron tensile testing machine to pull the bonded specimens at a 180° angle. The results, measured in grams/mm, unexpectedly indicated about a 32% improvement in peel strength with samples made from the coextruded modified polyester, as described in this invention, as compared to the control (141.4 g/mm versus 107.3 g/mm).

Example 5 - Films were coextruded as described in Example 2. A control sample was also prepared as described in Example 2. The films were heat sealed and tested as described in Example 4. The results unexpectedly showed about a 36% increase in peel strength with samples made from the coextruded modified polyester, as described in this invention, as compared to the control (136.5 g/mm versus 100.4 g/mm).

Example 6 - Films were coextruded as described in Example 3. A control sample was also prepared as described in Example 3. The films were heat sealed and tested as described in Example 4. The results surprisingly showed about a 327% increase in peel strength with samples made from the coextruded modified polyester, as described in this invention, as compared to the control (168.8 g/mm versus 39.5 g/mm). This significant increase in peel strength was totally unexpected.

Example 7 - A 10-mil film was extruded from Polyester A, a crystallizable polyester. One mil (\(0.001\)) of Polyester B was coextruded on each side of
the 10-mil film. A control sample was also prepared as described in Example 1.

The films were heat sealed and tested as described in Example 1. The results unexpectedly showed about a 55% increase in peel strength with samples made from the coextruded modified polyester, as described in this invention, as compared to the control (148.8 g/mm versus 96.1 g/mm).

Example 8 — A 6-mil film was extruded from Polyester A, a crystallizable polyester. Three mils (0.003") of Polyester B was coextruded on each side of the 6-mil film. A control sample was also prepared as described in Example 3.

The films were heat sealed and tested as described in Example 1. The results unexpectedly showed about a 353% increase in peel strength with samples made from the coextruded modified polyester, as described in this invention, as compared to the control (223.9 g/mm versus 49.5 g/mm).

Example 9 — A 10-mil film was extruded from Polyester A. One mil (0.001") of a modified copolyester, containing about 100 mol % terephthalic acid, about 85 mol % ethylene glycol and about 15 mol % 1,4-cyclohexanedicarboxylic acid, was coextruded on each side of the 10-mil film. A control sample was also prepared as described in Example 1.

The films were heat sealed and tested as described in Example 4. The results unexpectedly showed about a 99% increase in peel strength with samples made from the coextruded modified polyester, as described in this invention, as compared to the control (213.5 g/mm versus 107.3 g/mm).

Example 10 — A 6-mil film was extruded from Polyester A. Three mils (0.003") of a modified copolyester, as described in Example 9, was coextruded
on each side of the 6-mil film. A control sample was also prepared as described in Example 3.

The films were heat sealed and tested as described in Example 4. The results unexpectedly showed about a 252% increase in peel strength with samples made from the coextruded modified polyester, as described in this invention, as compared to the control (139.0 g/mm versus 39.5 g/mm).

**Example 11** – Film samples as prepared in Example 1, with a control sample consisting of Polyester A, coextruded with an amorphous copolyester (Polyester D), were put through a regrind operation for the purpose of conducting drying evaluations. The regrind had a bulk density of 15-22 lb/ft³, compared to 55 lb/ft³ for virgin crystallizable polyester pellets, which have already been crystallized. Regrind from each film sample was tumble blended with the virgin crystallizable polyester pellets, using a 50/50 weight ratio of regrind to pellets in the mixture. A ConAir crystallizer/dryer hopper utilizing desiccant air at 300°F was used to evaluate the drying and recrystallizing of the amorphous regrind mixed with virgin crystallizable polyester pellets. The evaluation unexpectedly showed that modified copolymers that show a melting heat of fusion greater than 0.5 cal/g (as measured in a DSC at 20°C/min) will not stick in a dynamic dryer set at crystalline polyester drying temperatures. The highly modified control regrind sample, which showed no melting heat of fusion, stuck together and prevented plug flow of the material through the hopper, which is highly undesirable.

**Example 12** – Single layer films were prepared using a 3.5" Welex extruder and a 3 roll stack nip polish take-up unit. The films were 50 mils (0.050") in thickness and consisted of the modified copolyester,
containing about 100 mol % terephthalic acid, about 88 mol % ethylene glycol and about 12 mol % 1,4-cyclohexanediol, and Polyester C as the control.

An internal test has been developed to measure the force and energy required to cut through a plastic film sample. An Instron tensile/compression testing machine has been outfitted with a compression load cell and a jig to hold a typical steel rule blade. The blade is pushed into the plastic while the force is monitored. Results of this test unexpectedly showed that it took about 9% less force and about 16% less energy for the modified polyester to be cut, as compared to the control (753 lb versus 826 lb and 1.51 ft-lb versus 1.79 ft-lb).

Example 13—The samples for Polysters B–H were prepared as in Example 1.

(1) The samples were melted to remove the existing crystallinity. The polymer samples were placed between two microscope cover glasses (thin slips of glass approximately 1 inch square) on a temperature-controlled hot plate for a predetermined time, usually a minute or two;

(2) The samples were quenched to the glassy state (below the glass transition temperature rapidly enough to prevent crystallization). Using forceps, the sample-cover glass sandwich, was rapidly transferred to a metal block which is at room temperature;

(3) The samples are crystallized at a predetermined temperature. The equipment or "sandwich" of (2) is transferred to the heated sample holder;

(4) The data is collected by recording the transmitted light intensity versus time;

(5) The data is analyzed. The time is recorded at which the transmitted intensity is half the maximum
Inherent viscosity (I.V.) is determined herein using 0.50 grams of polymer per 100 mL of a solvent consisting of 60% by weight phenol and 40% by weight tetrachloroethane.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.
The claims defining the invention are as follows:

1. A non-oriented layered film comprising
   (a) a first amorphous crystallisable polyester layer consisting essentially of polyethylene terephthalate having a melting point greater than about 238°C and a heat of fusion of greater than about 9 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20°C/min, and
   (b) a second amorphous, heat-sealing polyester layer consisting essentially of repeat units from terephthalic acid, about 85-93 mol % ethylene glycol and about 15-7 mol % cyclohexanedimethanol, said second polyester having a heat of fusion of greater than about 0.5 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20°C/min, the total thickness of said second polyester layer being less than about 50% of the total thickness of said film.

2. The film according to claim 1 wherein said heat-sealing layer is present on both sides of said first polymer layer.

3. The film according to claim 2 wherein said second polyester layer is about 5% to less than about 50% of the total thickness of said film.

4. The film according to claim 1 wherein said second polyester layer is about 5% to less than about 50% of the total thickness of said film.

5. The film according to claim 1 wherein said second heat-sealing polyester layer consists essentially of repeat units from terephthalic acid, about 87-91 mol % ethylene glycol and about 13-9 mol % cyclohexanedimethanol.

6. A package comprising the film according to claim 1.

7. A molded article comprising the film of claim 1.

8. The film according to claim 1 wherein said layers are coextruded.

9. The film according to claim 1 wherein at least one of said layers is preformed and the other layer is applied to the preformed layer as a coating.

10. A non-oriented polyester film consisting essentially of an amorphous, heat-sealing polyester wherein said heat-sealing polyester consists essentially of repeat units from terephthalic acid, about 85-93 mol % ethylene glycol and about 15-7 mol % cyclohexanedimethanol wherein said heat-sealing polyester has a heat of fusion of greater than about 0.5 cal/g as measured by a differential scanning calorimeter using a scan rate of about 20°C/min.
11. The film according to claim 10 wherein said second heat-sealing polyester consists essentially of repeat units from terephthalic acid, about 87-91 mol % ethylene glycol and about 13-9 mol % cyclohexanediol ethanol.

12. A package comprising the film according to claim 10.

13. A molded article comprising the film of claim 10.

DATED: 10 September, 1996

EASTMAN CHEMICAL COMPANY

By their Patent Attorneys

PHILLIPS ORMONDE & FITZPATRICK
Fig. 1

HALF-TIME (MIN.)

DEGREES (C)

POLYESTER D

POLYESTER E

SUBSTITUTE SHEET (RULE 28)
CRYSTALLIZATION HALFTIME (MIN.)

Fig. 2

CHDM LEVEL (MOL %)

130 DEG. C
140 DEG. C
160 DEG. C
150 DEG. C
INTERNATIONAL SEARCH REPORT

PCT/US 94/11348

A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<td>US,A,4 765 999 (WINTER) 23 August 1988 cited in the application</td>
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<td>EP,A,0 517 171 (DU PONT-MITSUI POLCHEMICALS CO., LTD.) 9 December 1992</td>
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

Date of the actual completion of the international search

17 January 1995

Date of mailing of the international search report

31.01.95

Name and mailing address of the ISA

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Fax (+31-70) 340-3016

Authorized officer

De Jonge, S
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<td>WO,A,91 08107 (EASTMAN KODAK COMPANY) 13&lt;br&gt;June 1991&lt;br&gt;see claims 1-5; example 2&lt;br&gt;see page 5, line 20 - line 23</td>
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