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| (54) Title: POLYOLEFIN WITH GOOD ADHESION PROPERTIES (57) Abstract A modified polyolefin which has good adhesion properties with regard to metals and to the surfaces of materials containing polar groups. The polyolefin contains 80-90.8 % polyolefin (LDPE, LLDPE, HDPE, PP or their copolymers or polymer mixtures), 0.01-10 % alkoxy silane and 0.01-10 % long-chain fatty acid for improving the adhesion properties. The alkoxy silane is grafted to the polyolefin with the aid of a free radical former, or the alkoxy silane has been added to the polyolefin without grafting. The long-chain fatty acid is stearic acid, myristic acid, behenyllic acid, oleic acid, linolic acid, linolenic acid or ricinolic acid. The alkoxy silane is vinyltrimethoxy silane, vinyltriethoxy silane, vinyltris (betamethoxyethoxy) silane or gammamethacrylopropyltrimethoxy silane. | | |

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Polyolefin with good adhesion properties

The present invention concerns a modified polyolefin with good adhesion properties towards metals and towards the surfaces of substances containing polar groups.

5 The known drawbacks of polyolefins, such as polyethylene and polypropylene, include the fact that their adhesive capacity to metals and to polar polymers is poor. Attempts have been made to improve the adhesivity by many different methods. As examples may be mentioned the treatment of the surface of polyolefins with acid,
10 with a flame or with a corona discharge, or by using adhesives such as ethylene/acrylic acid copolymers interposed between the polyolefin and the substrate in question. The adhesivity of polyolefins to polar polymers has also been improved by admixing thereto a polymer with good adhesion or by copolymerising polyethylene with comonomers containing functional groups.
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Functional groups giving better adhesiveness may also be produced by grafting various polar compounds to the polyolefin chains, such as acrylic acid, methacrylic acid and their
20 derivatives (e.g. salts), and maleic anhydride.

The observation is made in the Finnish patent application No. 813385 that it is also possible by grafting silanes with polyolefins to obtain good adhesion to metals (e.g. aluminium) and
25 to polar plastics (e.g. polyester and polyamide). Silane-modified polyolefin can be produced from high pressure polyethylene (LDPE), low pressure polyethylene (HDPE, LLDPE), polypropylene (PP) or their copolymers and from homopolymer/copolymer mixtures by admixing to them 0.01-10 % by weight unsaturated alkoxy silane and
30 0.01-0.5 % by weight of a radical former. The grafting may take place before or in connection with the processing step.

The silane to be grafted to polyolefin may be any unsaturated



alkoxysilane appropriate to the purpose. Such are e.g. vinyl-trimethoxysilane, vinyltriethoxysilane, vinyltris(betamethoxyethoxy)silane, or gammamethacryloxypropyltrimethoxysilane. It is possible for radical former to use any substance which forms radicals at the processing temperature but not at the homogenizing stage in the compound manufacturing. Such substances are e.g. peroxide compounds, such as dicumylperoxide.

Hydrolysable alkoxysilanes were originally developed for improving the miscibility of polymers and inorganic fillers (to serve as coupling agents). In the present case the alkoxy groups of the silanes are hydrolysed to hydroxy groups, and thereafter ensues condensation with the hydroxyl groups on the surface of the fillers. In addition to the alkoxy groups there is a group (there are groups) having such a chemical composition that it is (they are) well miscible with the polymer. Since the alkoxy groups of the silanes condensate under effect of water (and of a catalyst, e.g. dibutylstannic dilaurate), one has begun to use silanes in cross-linking techniques. This idea is based on unsaturated alkoxy silane being grafted with the aid of peroxide to the polymer, and cross-linking does not take place until after completion of the finished product, with the aid of water or steam. It is possible in this way to machine the polymer at high temperatures without risk of cross-linking, and the cross-linking step is also less expensive as regards both energy expenditure and investments. When silanes are used towards cross-linking, a condensing catalyst must always be present. In the Dow Corning system, two polymer mixes (silane-grafted LDPE and LDPE containing catalyst) are added into a conventional cable extruder, while in Maillefer's system all raw material components are directly added into a cable extruder of special design, wherein the grafting takes place. It has been noted in connection with cable manufacturing that certain silane-grafted LDPE brands adhere to aluminium.

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However, certain drawbacks are associated with the use in grafting of radical formers such as peroxides. Peroxides cause also cross-



linking in addition to grafting, whereby the melt index goes down and gels are produced. This is very objectionable in film applications. If the peroxides could be altogether omitted from the polyolefin formulation and adequate adhesion characteristics with regard to metals and polar plastics could still be achieved, a major advantage would be gained in film applications.

The object of the invention is to provide a modified polyolefin containing silane having good adhesion properties with regard to metals and polar plastics and in which the silane must not necessarily be grafted to the polyolefin by using radical formers. The modified polyolefin of the invention is characterized in that it contains 80-99.8 % polyolefin (LDPE, LLDPE, HDPE, PP or copolymers or polymer mixtures of these), 0.01-10 % alkoxysilane and 0.01-10 % carboxylic acid in order to improve the adhesion properties.

Grafting with silane improves in itself the adhesion of a polyolefin to metals and to polar plastics. Even in the case that the silane has not been grafted, i.e. the peroxide has been left out, adequate adhesion to polyamide and polyester can be achieved. The possibility of omitting the peroxide is a major advantage from the viewpoint of manufacturing and of the end product's other characteristics.

The modified polyolefin of the invention may be manufactured from high pressure polyethylene (LDPE), low pressure polyethylene (HDPE, LLDPE), polypropylene (PP) or from their copolymers or from mixtures of their homopolymers and copolymers.

When exceedingly good adhesivity is required and when gels are not objectionable (coating of metals, dyed products or thick-walled products), the alkoxysilanes may be grafted to the polyolefin chain by using 0.01-0.5 % by weight of a radical former (such as dicumyl peroxide). Grafting may take place either before the processing step or in connection therewith. When silane is grafted to a polyolefin chain, the alkoxysilane must contain an unsaturated



group. Silanes of this kind are, for instance, vinyltrimethoxy-silane, vinyltriethoxysilane, vinyltris(betamethoxyethoxy)silane or gammamethacryloxypropyltrimethoxysilane.

- 5 The long-chain fatty acid may be any fatty acid having a hydro-carbon chain longer than five carbons. It may be saturated, un-saturated, polyunsaturated, branched or substituted. This group includes for instance myristic acid, stearic acid, behenylic acid, oleic acid, linolic acid, linolenic acid, ricinolic acid.

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It has been noted in connection with the patent application No. 813385 that polyolefin grafted with silane must not be treated too long at elevated temperatures. It has been found that the adhesion properties can be optimized with regard to the temperature and delay time in the extruder. The heat treatment of silane-grafted polyolefin can be minimized by allowing the grafting to take place only at the processing step. It is possible to dissolve the radical former in silane and either to process the mixture of polyolefin, silane and radical or first to prepare a compound at a temperature so low that no grafting takes place. When the silane-grafted polyolefin contains a long-chain fatty acid, the adhesive properties depend in the same way on the extruder temperature and the delay time. Also in the absence of peroxide the adhesive properties of mixtures of polyolefin, silane and fatty acid depend on the extruder temperature and on the delay time. The lower the delay time, the better the adhesive properties. However, when the plastic courses become joined, the temperature must be as high as possible and the delay time at high temperature and high pressure as long as possible in order that sufficient adhesion might be achieved.

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The modified polyolefin of the invention may be used in various ways in applications in which good adhesion to polyamide and to other materials containing polar groups is implied. Of such uses may be mentioned for instance the coating of polyamide tubes and bottles directly with modified polyolefin, or the use of modified polyolefin as an intermediate or adhesive layer when

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coating polyamide tubes, bottles or other objects. Moreover, there
may be mentioned the use of polyolefin according to the invention
as film which sticks to polyamide and to other polar surfaces and,
in addition, to the polyolefin itself. One may also contemplate
5 coextruded multi-ply films, such as combination films of polyamide
and modified polyolefin, and compound films of polyamide, modified
polyolefin and common polyolefin. It is thus understood that the
modified polyolefin of the invention may be applied as such or as
coating of other films or as adhesive agent between other films,
10 depending on the objective in each particular case. Aluminium,
steel and other metal tubes, sheet or other objects may be coated
with the modified polyolefin of the invention, or it may be used
as an intermediate substance. In these instances the silane must
usually be grafted to the polyolefin.

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The invention is more closely described in the non-restrictive
examples following hereinafter. From silane-modified polyolefins,
strips were run with a Brabender extruder having 19 mm screw
diameter, length 20 L/D and compression ratio 3/1. The temperature
20 in the extruder was 120-130-140°C and the speed of the screw was
30 r.p.m. The delay time was then 110 seconds. The influence of
temperature (120-150-170°C; 130-170-200°C) and of the delay time
(110 s - 250 s) on the adhesion was also studied. The polyolefins
used in the experiments were LDPE polyethylene by Neste Oy (melt
25 index = 4 g/10 min, density = 0.922 g/cm³), the HDPE brand
HOSTALEN GD7255, manufactured by Hoechst (melt index = 5 g/10 min,
density = 0.955 g/cm³) and the EVA brand ESCORENE ULTRA 00220 by
Esso (melt index = 2 g/10 min, density = 0.941 g/cm³, vinyl acetate
content = 20 %). Dicumyl peroxide (DCP) was used for radical former,
30 and for silane were used vinyltrimethoxysilane (VTMO) and vinyltris-
(betamethoxyethoxy)silane (VTMOEO). The long-chain fatty acids used
were myristic acid, stearic acid and behenyllic acid.

The strips were pressed into sheets with 1 mm thickness, at 140°C.
35 Thereafter, a polyamide film (PA-6), a silane-modified polyolefin
sheet and an aluminium sheet were pressed together at 210°C; in
the case of HDPE this was also done at 250°C. Joining by pressing



was also carried out with polyester sheet (PET) and steel sheet at 180°C and 210°C. In connection with the joining by pressure, pre-heating was given for 90 s, the pressure was raised in 30 s and it was kept at joining pressure height (20 bar) for 40 s. From the specimens thus produced, five test samples were cut, which had width 20 mm and length 125 mm. The samples were stored for three days at 23°C and 50 % R.H. The tensile strength reflecting the adhesion was measured with an Instron tension testing apparatus, employing the pulling rate of 100 mm/min. The force required for detaching the different layers could be read from the recorder graph, and the adhesion in Ncm^{-1} could be calculated therefrom.

Example I

- 15 The effect of stearic acid on the adhesivity to polyamide of LDPE grafted with vinyltrimethoxysilane was studied. The radical former used in the grafting step was 0.05 % of dicumylperoxide (DCP).
- 20 Table 1 below shows that even minor stearic acid additions clearly improve the adhesion to polyamide. The adhesion increases with increase of the stearic acid quantity from 1 to 25 %, whereafter there is no further improvement of adhesion, or indeed a reduction.



TABLE 1: Effect of stearic acid on the adhesion to polyamide of LDPE grafted with vinyltrimethoxysilane (VTMO). Dicumylperoxide (DCP) used as peroxide.

| Exper- iment | VTMO (%) | DCP (%) | Molar ratio DCP/VTMO | Stearic acid (%) | Adhesion (N/cm) | |
|-----------------|-------------|------------|-------------------------|---------------------|--------------------|------|
| 5 | 1 | 2,5 | 0,02 | 0,005 | - | 5,0 |
| 10 | 2 | 2,5 | 0,02 | 0,005 | 0,05 | 7,8 |
| | 3 | 2,5 | 0,02 | 0,005 | 0,10 | 8,5 |
| | 4 | 2,5 | 0,02 | 0,005 | 1 | 12,8 |
| | 5 | 2,5 | 0,02 | 0,005 | 2 | 11,3 |
| | 6 | 2,5 | 0,02 | 0,005 | 3 | 9,7 |
| 15 | 7 | 3,0 | 0,05 | 0,010 | - | 8,5 |
| | 8 | 3,0 | 0,05 | 0,010 | 0,05 | 9,0 |
| | 9 | 3,0 | 0,05 | 0,010 | 0,10 | 9,1 |
| 20 | 10 | 3,0 | 0,05 | 0,010 | 1 | 14,4 |
| | 11 | 3,0 | 0,05 | 0,010 | 2 | 16,3 |
| | 12 | 3,0 | 0,05 | 0,010 | 3 | 12,5 |

Example II

25 The effect of stearic acid on the adhesion of polyethylene to polyamide was studied in the case that the silane was not grafted to the polyethylene chain at all. Table 2 below reveals that a small amount of stearic acid improves the adhesion to polyamide of vinyltrimethoxysilane-modified polyethylene. The extruder

30 temperature has to be comparatively low; this may be due to the circumstance that VTMO evaporates if the temperature is excessive (boiling point 120°C). The delay time in the extruder should also be comparatively short (2-3 minutes).

35 It is further readable in Table 2 that stearic acid alone or VTMO alone do not cause any improvement in the adhesion to polyamide: both components must be present (when no grafting has been applied).



TABLE 2: Effect of stearic acid on the adhesion to polyamide of LDPE admixed with vinyltrimethoxysilane. No peroxide used.

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| Exper- iment | VTMO (%) | Ultimate ex- truder temp. (°C) | Delay time in extruder (s) | Stearic acid (%) | Adhesion (N/cm) | |
|-----------------|-------------|--------------------------------------|----------------------------------|------------------------|--------------------|-----|
| 10 | 13 | 3,0 | 140 | 110 | 0,5 | 0 |
| | 14 | 3,0 | 140 | 210 | 0,5 | 0 |
| | 15 | 3,0 | 140 | 250 | 0,5 | 0 |
| | 16 | 3,0 | 140 | 110 | 1,0 | 6,8 |
| | 17 | 3,0 | 140 | 210 | 1,0 | 3,6 |
| 15 | 18 | 3,0 | 140 | 250 | 1,0 | 1,4 |
| | 19 | 3,0 | 170 | 110 | 1,0 | 0 |
| | 20 | 3,0 | 200 | 110 | 1,0 | 0 |
| | 21 | - | 140 | 110 | 1,0 | 0 |
| | 22 | 3,0 | 140 | 110 | - | 0 |

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Example III

The effect on adhesion to polyamide and to aluminium exerted by various polyolefins, silanes and long-chain fatty acids was studied. Such specimens were made in which the silane was grafted to the polyolefin and which contained or did not contain fatty acid. In addition there are specimens to which silane and fatty acid were added but no peroxide.

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The results stated in Table 3 below illustrate the adhesion-improving effect of a long-chain fatty acid. This is evident with particular clarity in the case of HDPE, which had no adhesion to polyamide or to aluminium when grafted with silane. Good adhesion to polyamide was achieved with stearic acid addition (1 %) and a nearly equally good adhesion even in the case in which the peroxide was left out. However, no improvement of the adhesivity

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to aluminium was achieved in this case.

TABLE 3: Effect of fatty acids on the adhesion to polyamide and to aluminium of polyolefin admixed with alkoxysilane.

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| Exper- iment | Poly- mer | Silane | DCP (%) | Fatty acid | Pressing temper- ature (°C) | Adhesion (N/cm) | |
|-----------------|--------------|-----------|------------|------------------|--------------------------------------|-----------------|-------|
| | | | | | | PA | Al |
| 23 | LDPE | 3% VTMOEO | 0,05 | - | 210 | 9,6 | 19,2 |
| 24 | LDPE | 3% VTMOEO | 0,05 | 1% Stearic acid | 210 | 18,1 | 1,2 |
| 25 | LDPE | 3% VTMOEO | - | 1% Stearic acid | 210 | 1,1 | 0 |
| 26 | HDPE | 3% VTMO | 0,05 | - | 210/250 | 0/11 | 0/13 |
| 27 | HDPE | 3% VTMO | 0,05 | 1% Stearic acid | 210/250 | 30,5/51,3 | 0/1,1 |
| 28 | HDPE | 3% VTMO | - | 1% Stearic cid | 210/250 | 32,1/52,6 | 0/0 |
| 29 | EVA | 3% VTMO | 0,05 | - | 210 | 35,2 | 72,3 |
| 30 | EVA | 3% VTMO | 0,05 | 1% Stearic acid | 210 | 86,3 | 91,7 |
| 31 | EVA | 3% VTMO | - | 1% Stearic acid | 210 | 1,0 | 0 |
| 32 | LDPE | 3% VTMO | 0,05 | 1% Myristic acid | 210 | 14,3 | 0 |
| 33 | LDPE | 3% VTMO | - | 1% Myristic acid | 210 | 6,0 | 0 |
| 34 | LDPE | 3% VTMO | 0,05 | 1% Behenylic ac. | 210 | 12,6 | 1,7 |
| 35 | LDPE | 3% VTMO | - | 1% Behenylic ac. | 210 | 0,2 | 0 |

Example IV

A study was made in this example of the kind of adhesion values obtained by mixing together LDPE, VTMO and stearic acid in one case and dicumyl peroxide in one case, in a "Buss-Co-Kneader PR 46" mixer at low temperature (below 125°C). Of each formulation 20 kg were made. Sheets were pressed in the manner described, the joining pressing temperature being 210°C, and the adhesion to polyamide and to aluminium was tested. The joined sandwich specimens were also kept in boiling water for one hour, followed by adhesion testing again. With modified LDPE and polyamide also



two-layer coextrusion by the film blowing method was carried out. The ultimate temperature of the silane-modified LDPE was 190°C and that of the polyamide, 240°C, and the molten polymers combined in the nozzle. Since there was rather little silane-modified LDPE and the coextrusion line was rather primitive, uniform conditions and films with uniform thickness were hard to achieve. However, the observation can be made from these films that by using 3 % VTMO and 1 % stearic acid in the LDPE so good adhesion to the polyamide course was achieved that the courses could not be separated.

It is also noted that no gels occurred in the LDPE modified in this manner. In contrast, those formulations which contained dicumylperoxide gave rise to gels, and the adhesion was weaker. The conditions in which the polymer courses became joined (in this case also the polyamide is in molten state) had a powerful effect on the adhesion properties of the polyolefins modified with different silanes. When also sandwich compounds were pressed from equivalent modified brands with polyamide and with aluminium, results were obtained which are similar to those already reported. Stearic acid improved the adhesion to polyamide of VTMO-grafted polyolefin, and a lesser yet good enough adhesion was also attained by using VTMO and stearic acid without peroxide. In this case adhesion to aluminium was also obtained. When the pressed sandwich specimens were boiled in water for one hour, similar results were also obtained, although the adhesion was slightly lower.



TABLE 4: The LDPE/VTMO/stearic acid mixtures prepared with the Buss-Co-Kneader PR 46, and their adhesions to polyamide and to aluminium.

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| Experiment | VTMO (%) | DCP (%) | Stearic acid (%) | Adhesion (N/cm) | | Behaviour in trial extrusion | Adhesion sequence |
|------------|----------|---------|------------------|-----------------|-----------|-------------------------------|-------------------|
| | | | | PA | Al | | |
| | | | | x) | x) | | |
| 36 | 3 | 0,05 | - | 9,5/5,3 | 14,6/9,6 | Gels | III |
| 37 | 3 | 0,05 | 1 | 13,5/9,0 | 12,2/11,0 | Gels | II |
| 38 | 3 | - | 1 | 5,8/1,7 | 2,8/2,7 | No gels | I |
| | | | | | | Layers could not be separated | |

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x) Kept in boiling water for 1 h.

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Example V

The adhesion was studied in the case that LDPE modified with VTMO and stearic acid is pressed onto polyester (PET) and steel. Two different temperatures were used in the pressing step (180°C and 210°C). Table 5 below reveals that good adhesion both to polyester and to steel was obtained by grafting VTMO to LDPE. Lowering of the pressing temperature to 180°C caused the adhesions to be reduced, but they were still fairly good. On addition of stearic acid, the adhesions both to polyester and to steel were reduced, and when moreover the peroxide was omitted, they were even further impaired.

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TABLE 5: Effect of stearic acid on the adhesion to LDPE admixed or grafted with vinyltrimethoxysilane (VTMO).

| 5 Experiment | VTMO (%) | Molar ratio DCP/VTMO | Stearic acid (%) | Adhesion (N/cm) | | | |
|-----------------|----------|----------------------|------------------|-----------------|-------|----------|-------|
| | | | | PET | | FE | |
| | | | | 180°C | 210°C | 180°C | 210°C |
| 39 | 3 | 0,010 | - | 4,2/10,3 | | 9,6/19,2 | |
| 10 40 | 3 | 0,010 | 1 | 0 / 4,6 | | 0 / 1,2 | |
| 41 | 3 | - | 1 | 0 / 1,7 | | 0 / 0 | |

Example VI

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In this example was studied the pressing to polyester (PET) and to steel of EVA modified with VTMO and stearic acid. Two different pressing temperatures (180°C and 210°C) were used. Table 6 reveals that by grafting VTMO to EVA very good adhesion both to polyester and

25 to steel is achieved. The adhesions became less on lowering the pressing temperature to 180°C but were excellent all the same. When stearic acid was added, the adhesion both to polyester and to steel was weakened, and when furthermore the peroxide was omitted from the formulation, even lower adhesion values were found. When the

30 basic polymer was EVA, better adhesions were obtained with all formulations than in the case of LDPE.



TABLE 6: Effect of stearic acid on the adhesion to steel and polyester of EVA (ESCORENE UL 00220, 20 % VA) admixed or grafted with vinyltrimethoxysilane (VTMO).

| Exper- iment | VTMO (%) | Molar ratio DCP/VTMO | Stearic acid (%) | Adhesion (N/cm) | | | |
|-----------------|-------------|-------------------------|---------------------|-----------------|-------|-------|-------|
| | | | | PET | | FE | |
| | | | | 180°C | 210°C | 180°C | 210°C |
| 42 | 3 | 0,010 | - | 42,3 | 147,1 | 17,3 | 96,2 |
| 43 | 3 | 0,010 | 1 | 18,3 | 38,1 | 2,1 | 4,2 |
| 44 | 3 | - | 1 | 0 | 3,4 | 0 | 2,3 |

Example VII

The adhesion of two commercial adhesion plastic brands (Plexar P-1 and Surlyn A 1650) to polyamide, aluminium, polyester and steel was studied, with pressing temperature 210°C. The results in Table 7 reveal that Plexar P-1 yields better adhesion with these materials than Surlyn A 1650. These brands are also characterized by excellent adhesion to metals, especially to steel. The adhesions to polyester, again, are lower than those to polyamide. The adhesions to polar plastics are of such order that the same results are achievable by modifying polyolefins with silanes and long-chained fatty acids.

TABLE 7: Adhesions to polyamide, aluminium, polyester and steel of competing polymer brands.

| Exper- iment | Brand | Adhesion (N/cm) | | | |
|-----------------|---------------|-----------------|-----------|-----------|-------|
| | | Polyamide | Aluminium | Polyester | Steel |
| 45 | Plexar P-1 | 18,1 | 29,8 | 10,4 | 68,3 |
| 46 | Surlyn A 1650 | 11,3 | 17,3 | 2,3 | 23,2 |

Example VIII

Since polyolefins modified with silane as taught by the invention will be used for instance as adhesive layer in coextrusion, coextruded strips were made as follows.

The formulation stated below were run with a Brabender extruder as dry mixes with temperature profile 120°C, 150°C, T°C and with screw speed 30 r.p.m., and into the two-layer extruder was urged with nitrogen gas, polar plastic (polyamide-6 or EVAL-F ethylene/vinylalcohol copolymer) at T°C so that the silane-modified polyolefin and the polar plastic combined 1 cm before the exit from the strip nozzle. The adhesion characteristics of the coextruded strips were thereafter examined in an Instron tension testing apparatus, the results being compiled in Table 8.

TABLE 8: Adhesions of coextruded strips

| Test | Quality 1 | Quality 2 | T(°C) | Adhesion (N/cm) |
|------|--|-----------|-------|-----------------|
| 45 | LDPE + 1% VTMO + 0.05% DCP + 1% isostearic acid | PA-6 | 250 | f |
| 46 | LDPE + 3% VTMO + 0.05% DCP + 1% Edenor UKD | PA-6 | 250 | 14.9 |
| 47 | LDPE + 3% VTMO + 0.05% DCP + 1% Edenor C 6 R | PA-6 | 250 | 13.8 |
| 48 | LDPE + 3% VTMO + 0.05% DCP | PA-6 | 250 | 5.2 |
| 49 | LDPE + 3% VTMO + 0.05% DCP + 0.1% H ₂ O | PA-6 | 250 | 1 |
| 50 | LDPE + 3% VTMO + 0.05% DCP + 0.2% dibutyl tin dilaurate | PA-6 | 250 | 1 |
| 51 | LDPE + 3% VTMO + 1% adipinic acid | PA-6 | 250 | 3.1 |
| 52 | LDPE + 1.5% VTMO + 0.02% DCP + 0.05% isostearic acid | EVAL-F | 210 | f |
| 53 | Sioplas E | PA-6 | 250 | 1 |

- f = plastic layers could not be separated
l = plastic layers were completely separate
Edenor UKD \approx conjugated C₁₈, technical fatty acid quality by Henkel
Edenor C 6 R \approx C₆, technical fatty acid quality by Henkel
5 EVAL-F = ethylene/vinylalcohol copolymer, Kuraray

Table 8 reveals that carboxylic acid improves the adhesion properties of silane-modified polyolefin also in coextrusion with a polar plastic. This test is better consistent with actual
10 conditions in the sense that the pressing time is very short but the temperature high. With isostearic acid so good adhesion is achieved in this way that it cannot be measured. With other acids adhesion is also obtained, even when the silane has not been grafted. The example also demonstrates how hydrolysis of grafted
15 silane prevents the forming of adhesion. The hydrolysis of silane is accelerated when water and/or a condensation catalyst is present, and already grafted silane (Sioplas E) is readily hydrolysed.



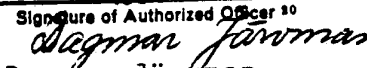
Claims

1. A modified polyolefin with good adhesion properties towards metals and towards the surfaces of materials containing polar groups, characterized in that it contains 80-99.8 % polyolefin (LDPE, LLDPE, HDPE, PP or their copolymers or polymer mixtures),
5 0.01-10 % alkoxysilane and 0.01-10 % carboxylic acid in order to improve the adhesion properties.
2. Polyolefin according to claim 1, characterized in that
10 alkoxysilane has been grafted to polyolefin in a manner known in itself with the aid of a free radical former.
3. Polyolefin according to claim 1, characterized in that
alkoxysilane has been added to polyolefin without grafting.
- 15 4. Polyolefin according to any one of claims 1-3, characterized in that the carboxylic acid consists of a saturated, unsaturated, or polyunsaturated hydrocarbon chain or a derivative thereof.
5. Polyolefin according to any one of claims 1-4, characterized
20 in that the carboxylic acid is caproic acid, lauric acid, lauroleic acid, myristic acid, stearic acid, isostearic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, behenic acid, erucic acid, adipinic acid, azelaic acid.
- 25 6. Polyolefin according to any one of claims 1-5, characterized in that the alkoxysilane is vinyltrimethoxysilane, vinyltriethoxysilane, vinyltri(beta-methoxyethoxy)silane or gamma-methacryloxypropyltrimethoxysilane.



INTERNATIONAL SEARCH REPORT

International Application No **PCT/FI84/00015**

| 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 ³ C 08 F 255/00, C 08 F 8/46 | | | | | | | |
|---|--|-------------------------------------|---|--|----------------------------|-------|-------------------------------|
| II. FIELDS SEARCHED <div style="text-align: right; margin-right: 50px;">Minimum Documentation Searched ⁴</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 25%;">Classification System</th> <th style="width: 75%;">Classification Symbols</th> </tr> </thead> <tbody> <tr> <td style="padding: 2px;">IPC 3</td> <td style="padding: 2px;">C 08 F 255/00; C 08 F 8/46</td> </tr> <tr> <td style="padding: 2px;">US C1</td> <td style="padding: 2px;"><u>521:86</u>; <u>525:61</u></td> </tr> </tbody> </table> <div style="text-align: center; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴</div> | | Classification System | Classification Symbols | IPC 3 | C 08 F 255/00; C 08 F 8/46 | US C1 | <u>521:86</u> ; <u>525:61</u> |
| Classification System | Classification Symbols | | | | | | |
| IPC 3 | C 08 F 255/00; C 08 F 8/46 | | | | | | |
| US C1 | <u>521:86</u> ; <u>525:61</u> | | | | | | |
| SE, NO, DK, FI classes as above | | | | | | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ | | | | | | | |
| Category ⁵ | Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ | | | | | |
| X | DE, A1, 2 444 829 (HERMANN UWE VOIGT) 8 April 1976 & BE, 831461 NL, 7510938 FR, 2285419 US, 4048129 GB, 1500030 JP, 51050954 CA, 1061496 | 1-6 | | | | | |
| X | Chemical Abstracts, Vol 89(1978), abstract No 147611w, Nishizawa, Hitoshi; Kato Masahiro; Shimanuki, Horoshi; Suyama, Saichi | 1-6 | | | | | |
| X | Chemical Abstracts, Vol 98(1983), abstract No 108241s, Guede, I. Mueller, V. Tolstaya, S.N.; Kozlov, G.V; Jgnatkina, T.I. | 1-6 | | | | | |
| A | DE, A1, 2 611 491 (SHINKAI, KEN, HIRAKATA; CHIBA, NORIO, MUKOU; OZAKI, YUTAKA) 23 September 1976 <div style="text-align: right; margin-top: 10px;">.../...</div> | 1 | | | | | |
| <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> ¹⁵ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published 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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Δ" document member of the same patent family </td> </tr> </table> | | | ¹⁵ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | "T" later document published 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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Δ" document member of the same patent family | | | |
| ¹⁵ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | "T" later document published 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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Δ" document member of the same patent family | | | | | | |
| IV. CERTIFICATION | | | | | | | |
| Date of the Actual Completion of the International Search ¹⁹ <div style="text-align: center;">1984-10-16</div> | Date of Mailing of this International Search Report ²⁰ <div style="text-align: center;">1984-10-22</div> | | | | | | |
| International Searching Authority ¹ <div style="text-align: center;">Swedish Patent Office</div> | Signature of Authorized Officer ²⁰ <div style="text-align: center;">  Dagmar Järve </div> | | | | | | |

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

| Category * | Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No ¹⁸ |
|------------|--|------------------------------------|
| A | DE, B2, 2 151 270 (SCOTT, HENRY GEORGE, DINAS POWIS) 8 February 1979 | 1 |