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P/00/001 28/5/91
Section 29

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AUSTRALIA

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the person identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

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[70]	Nominated Person:	HOECHST AKTIENGESELLSCHAFT
	Address:	D-6230 FRANKFURT/MAIN 80, FEDERAL REPUBLIC OF GERMANY
[54]	Invention Title:	COPOLYMERS AND THEIR USE AS LUBRICANTS AND RELEASE AGENTS FOR PROCESSING THERMOPLASTICS
[72]	Name(s) of actual inventor(s):	FRANZ-LEO HEINRICHS, GERD HOHNER, ANTON LUKASCH AND JAN-PETER PIESOLD

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BASIC CONVENTION APPLICATION(S) DETAILS

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Drawing number recommended to accompany the abstract .....

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

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Darryl B. Mischlewski

Registered Patent Attorney

DATED this 26th day of November 1992

F039307 27/11/92

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

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NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **HOECHST AKTIENGESELLSCHAFT**, of D-65926 Frankfurt am Main, being the applicant in respect of Application No. 29729/92 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors by virtue of an employment contract between the inventors and the person nominated for the grant of the patent.

The person nominated for the grant of the patent is the applicant of the basic application listed on the patent request form.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

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Darryl B. Mischlewski
Registered Patent Attorney

DATED this 18th day of July, 1994

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COPOLYMERS AND THEIR USE AS LUBRICANTS AND RELEASE AGENTS FOR PROCESSING THERMOPLASTICS

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(56) Prior Art Documents
US 4399248
US 4184993

(57) Claim

1. A copolymer comprising
20 to 99.5 parts by weight of units which are derived from a C_{12}-C_{60}-α-olefin,
0.5 to 50 parts by weight of units which are derived from a carboxylic acid of the formula $CH_2=CR^1-COOH$,
0.1 to 60 parts by weight of units which are derived from a carboxylic acid ester of the formula $CH_2=CR^1-COOR^2$, in which formulae R^1 is a hydrogen atom or a methyl group and R^2 is a straight-chain or branched alkyl radical havingh 1 to 6 carbon atoms, and
0.0 to 30 parts by weight of units which are derived from styrene, 3-methylstyrene, 4-methylstyrene or α-methylstyrene.

6. A thermoplastic molding composition comprising 0.05 to 5% by weight, based on the molding composition, of a copolymer as claimed in claim 1.

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Regulation 3.2(2)

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653085

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:

Lodged:

Invention Title: COPOLYMERS AND THEIR USE AS LUBRICANTS AND RELEASE AGENTS FOR PROCESSING THERMOPLASTICS

The following statement is a full description of this invention, including the best method of performing it known to :-US

Description

Copolymers and their use as lubricants and release agents for processing thermoplastics

The present invention relates to copolymers of α-olefins, unsaturated carboxylic acids, unsaturated carboxylic acid esters and, if appropriate, styrene, and to the use of such copolymers as auxiliaries for processing thermoplastics.

Lubricants which on the one hand are said to improve the flow properties of the polymer melt and on the other hand are said to reduce the tendency of the melt to stick to the metallic components of processing machines are usually employed for processing thermoplastics. Lubricants have particular importance in the processing of polyvinyl chloride, since this plastic cannot be processed without lubricants because of its sensitivity toward exposure to high temperatures and toward shearing forces, as well as its pronounced tendency to stick.

A distinction is made between lubricants which are readily compatible with the polymer melt and therefore chiefly have the effect of improving flow (internal lubricants) and those which are incompatible to a greater or lesser degree, and therefore become enriched at phase boundaries and display, for example, a release action there (external lubricants).

A large number of inexpensive, readily accessible products are available for improving the flow properties of polyvinyl chloride melts. Examples which may be mentioned here are fatty alcohols, fatty acids, fatty acid partial esters and fatty acid amides.

The choice of suitable external lubricants for PVC presents problems, since these sometimes must meet contradictory requirements. In order to be active, suitable lubricants must have a certain incompatibility with the PVC melt, so that a film having a releasing action can form between the melt and the metal components of the processing machines. However, incompatible additives have the disadvantage that they often cause severe clouding on the end product. Given the numerous uses for which a highly transparent end product is desired, the permitted amount used of a release agent is therefore often limited to the extent that its action is no longer adequate. These problems have a particularly adverse effect in the production of thin PVC calendered film, since the tendency to stick and the low mechanical resistance of such films in the hot state requires the use of a large amount of lubricant for detachment from the rolls, but on the other hand particularly high transparency requirements are imposed on such films, for example in the packaging sector.

Known lubricants for the production of plasticizer-free PVC films are on the one hand montan wax and on the other hand practically neutral mixed esters of aliphatic, cycloaliphatic or aromatic dicarboxylic acids having 2 to 22 carbon atoms, aliphatic polyols having 2 to 6 hydroxyl groups and aliphatic monocarboxylic acids having 12 to 30 carbon atoms with hydroxyl or acid numbers of 0 to 6 (cf. GB 1,292,548), as well as practically neutral mixed esters of aliphatic diols, aliphatic, cycloaliphatic or aromatic polycarboxylic acids having 2 to 6 carboxyl groups and aliphatic monofunctional alcohols with 12 to 30 carbon atoms (cf. GB 1,450,273).

Soaps and soap esters which are prepared from long-chain carboxylic acids which are accessible by free radical addition of short-chain monocarboxylic acids, preferably of propionic acid, onto long-chain α-olefins having 22 to

100 carbon atoms are furthermore known (cf. US 4,029,682). Although the soaps and soap esters thus obtained are excellent lubricants and release agents for plastics processing, their preparation requires a two- or three-stage preparation process, which leads to these products becoming more expensive. It would therefore be advantageous if suitable lubricants and release agents could be arrived at directly in one reaction step.

Lubricants and release agents for chlorine-containing thermoplastics prepared by copolymerization of acrylic acid, acrylic acid esters, maleic acid or maleic acid esters with ethylene are also described (cf. US 4,438,008). Although these lubricants and release agents are accessible in one reaction step and have a good compatibility and release action in PVC, the copolymerization requires high pressures and temperatures, and therefore specifically designed apparatuses.

Finally, copolymers of α-olefins having more than 30 carbon atoms and maleic acid or maleic acid esters are known (cf. US 4,334,038). Although these lubricants are accessible in one reaction step without specifically designed apparatuses and have a high release action, they do not yet have an action in PVC which is universally satisfactory.

The montan waxes, which are very advantageous from the applications point of view, are limited to industrially demanding fields because of their high cost. The known mixed esters cause relatively severe clouding in modified polyvinyl chloride even at a lower dosage, and are unsuitable as lubricants and release agents for production of particularly high-quality low temperature (LT) films (®Luvitherm films), in which 2 to 4 parts of lubricant and release agent are employed per 100 parts of E-PVC.

There was therefore the object of providing lubricants and release agents which on the one hand have the positive properties of the montan waxes, such as, for example, their usability in LT films, and which on the other hand are accessible in a simple and economical manner.

To this end, there is provided a copolymer comprising

20 to 99.5 parts by weight of units which are derived from a C_{12}-C_{60}-α-olefin,

0.5 to 50 parts by weight of units which are derived from as carboxylic acid of the formula $CH_2=CR^1-COOH$,

0.1 to 60 parts by weight of units which are derived from a carboxylic acid ester of the formula $CH_2=CR^1-COOR^2$, in which formulae R^1 is a hydrogen atom or a methyl group and R^2 is a straight-chain or branched alkyl radical having 1 to 6 carbon atoms, and

0.0 to 30 parts by weight of units which are derived from styrene, 3-methylstyrene, 4-methylstyrene or α-methylstyrene.

The lubricants and release agents according to the invention are thus copolymers of α-olefins, unsaturated carboxylic acids and unsaturated carboxylic acid esters, and, if appropriate, vinylaromatic compounds of the styrene type.

Possible α-olefins are those having a chain length of 12 to 60, preferably 18 to 60, particularly preferably 24 to 60 carbon atoms. Both olefins having pure chains and olefin mixtures such as are obtained, for example, as distillation cuts or distillation residues in the known preparation processes can be employed. Industrial α-olefin mixtures, in particular those having a relatively high chain length, can contain, in addition to 1-alkenes, larger or smaller amounts of internal and lateral olefinic double bonds (vinylidene and vinylene groups).

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The unsaturated carboxylic acids employed according to the invention are compounds of the general formula $CH_2=CR^1-COOH$, in which R^1 is a hydrogen atom or a methyl group, i.e., for example, acrylic or methacrylic acid. The unsaturated carboxylic acid esters used are compounds of the general formula $CH_2=CR^1-COOR^2$, in which R^1 has the above meaning and R^2 is a straight-chain or branched alkyl radical having 1 to 6 carbon atoms. The methyl and ethyl esters of acrylic or methacrylic acid are preferred, and the methyl ester or acrylic acid is particularly preferred.

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Vinylaromatic compounds which can be employed are styrene, 3-methylstyrene, 4-methylstyrene or α-methylstyrene. It is also possible to employ several of the carboxylic acids, carboxylic acid esters and, if appropriate, styrenes mentioned.

The lubricants according to the invention are prepared in a manner which is known per se, by reaction of the starting monomers under the catalytic action of small amounts of organic peroxides in the presence or in the absence of an inert solvent. Polymerization in the absence of a solvent is preferred. A mixture of carboxylic acid, carboxylic acid ester and free radical initiator, for example, can be added dropwise, at elevated temperature and while stirring, to the α-olefin which has been initially introduced into the reaction vessel. When the reaction has ended, unreacted monomers and volatile dissociation products of the peroxide can be removed by distillation. Organic peroxides are preferably employed as the free radical initiators. The reaction temperature here is to be matched to the dissociation characteristics of the particular peroxide used. At a temperature of 100 to 160°C, for example, dialkyl peroxides, such as di-t-butyl peroxide, or diaroyl peroxides, such as dibenzoyl peroxide, are particularly suitable. The molar ratio of the monomer components and therefore the chemical build-up and the polarity of the copolymers can be adjusted within wide limits. There is therefore the possibility of matching the properties of the lubricant to the particular application requirements in an optimum manner.

The monomers are employed in the following ratios:

α-olefin	20 to 99.5, preferably 40 to 95% by weight,
unsaturated carboxylic acid	0.1 to 50, preferably 0.5 to 30% by weight,

unsaturated carboxylic acid ester	0.1 to 60, preferably 1.0 to 40% by weight,
styrene compound	0.0 to 30, preferably 0.0 to 20% by weight.

The reaction temperature is 70 to 180, preferably 90 to 160°C, the reaction pressure is 1.0 to 5.0, preferably 1.0 to 1.5 bar, and the reaction time is 0.5 to 20, preferably 1 to 7 hours.

The copolymers according to the invention are employed as lubricants and release agents in thermoplastic molding compositions, for example in polyvinyl chloride, which can be prepared by the known processes - for example suspension, bulk or emulsion polymerization - and copolymers of vinyl chloride with up to 30% by weight of comonomers such as, for example, vinyl acetate, vinylidene chloride, vinyl ethers, acrylonitrile, acrylic acid esters, maleic acid mono- or diesters or olefins, and in graft polymers of polyvinyl chloride and polyacrylonitrile. Polyvinyl chloride, polyvinylidene chloride, ethylene/vinyl acetate copolymers, polyacrylonitrile, copolymers of vinyl chloride and vinyl acetate, and graft polymers derived therefrom, or mixtures of the above-mentioned thermoplastics are preferred. Those copolymers according to the invention which have a low carboxylic acid content and a high ester content exhibit particularly advantageous properties when used for processing PVC. Too high a carboxylic acid content has an adverse effect on the color properties of the lubricants, especially in Ca/Zn-stabilized PVC. Because of its effect of increasing compatibility with the PVC, a high ester content leads to better transparency properties, better flow properties of the PVC melt and a shorter delay in plasticization of the PVC.

The amount added is 0.05 to 5% by weight, based on the polymer. If the molding composition is based on B- or

S-PVC, the amount added is preferably 0.05 to 1% by weight, and if it is based on E-PVC, the amount added is preferably 1.0 to 5, in particular 2 to 4% by weight, in each case based on the polymer. The copolymers according to the invention are mixed into the polymers in the customary manner during preparation or processing of the molding compositions.

In addition to the copolymers according to the invention, the plastics molding composition can additionally comprise fillers, heat stabilizers, light stabilizers, antistatics, flameproofing agents, reinforcing substances, pigments, dyestuffs, processing auxiliaries, lubricants, impact modifiers, antioxidants, blowing agents and optical brighteners in the customary amounts.

The examples which follow are intended to illustrate the invention.

The acid and hydrolysis numbers and the dropping points were determined by DGF standard methods M-IV 2 (57) and M-III 3 (75) respectively (standards of the Deutsche Gesellschaft für Fettwissenschaft e.V.). The melt viscosities were measured with the aid of a rotary viscometer.

Example 1

Preparation of a C_{24}-C_{60}-α-olefin/acrylic acid/methyl acrylate copolymer:

500 g of a commercially available C_{24}-C_{60}-α-olefin cut were initially introduced into a five-necked flask fitted with a thermometer, stirrer, dropping funnel and reflux condenser, and were heated to 140°C. A mixture of 219.0 g of methyl acrylate, 10.0 g of acrylic acid and 5.0 g of di-t-butyl peroxide was added dropwise at this temperature in the course of 5 hours, while stirring. When the dropwise addition had ended, the mixture was allowed to

after-react for a further 30 minutes, and volatile constituents were distilled off under a vacuum of about 15 mbar at a bath temperature of 170°C. The colorless reaction product, which solidifies in the form of a wax, was poured into dishes.

Physical data: acid number 11 mg of KOH/g; hydrolysis number about 160 mg of KOH/g; dropping point 70°C; melt viscosity 520 mPa.s (measured at 90°C).

Example 2

Preparation of a 1-tetradecene/acrylic acid/methyl acrylate copolymer:

196.0 g of 1-tetradecene, 131.7 g of methyl acrylate, 4.0 g of acrylic acid and 2.6 g of di-t-butyl peroxide were reacted with one another by a process analogous to that described in Example 1. The resulting colorless, semi-solid terpolymer had an acid number of 10 mg of KOH/g and a hydrolysis number of about 205 mg of KOH/g.

Example 3

Preparation of a C_{24}-C_{60}-α-olefin/acrylic acid/methyl acrylate/styrene polymer

500 g of C_{24}-C_{60}-α-olefin were reacted with a mixture of 175.0 g of methyl acrylate, 47 g of styrene and 16.0 g of acrylic acid in the presence of 5.0 g of t-butylbenzoate analogously to Example 1.

A colorless wax having the following characteristic data was obtained:
acid number 16 mg of KOH/g; hydrolysis number 161 mg of KOH/g; dropping point 72°C; melt viscosity 390 mPa.s (measured at 90°C).

Example 4

The copolymers according to Example 1, 2 and 3 were tested for their transparency properties in the following recipe. A commercially available montan acid ester was used for comparison.

S-PVC (K value about 60)	100 parts by weight
Processing auxiliary containing acrylate	1.0 part by weight
Octyltin stabilizer	1.5 parts by weight
Glycerol monooleate	0.3 part by weight
Test product	0.6 part by weight

These mixtures were plasticized on a roll mill at 190°C, and small sheets 0.5 and 2.0 mm thick were then pressed. These were tested with a transparency meter in neutral gray light.

Test product	Transparency in % 0.5 mm	2.0 mm
Copolymer I (according to Example 1)	76.8	66.7
Copolymer II (according to Example 2)	83.3	74.9
Copolymer III (according to Example 3)	83.7	67.5
Ethylene glycol montanate (Hoechst Wachs E)	69.6	41.6

Example 5

The copolymers according to Example 1, 2 and 3 were tested for their release action in the following test recipe:

B-PVC (K value about 57)	100 parts by weight
MBS impact modifier	8 parts by weight
Processing auxiliary containing acrylate	1.2 parts by weight
Thiotin stabilizer	1.6 parts by weight
Epoxidized soybean oil	1.0 part by weight

Glycerol monooleate	0.3 part by weight
Test product	0.6 part by weight

Testing was carried out on a roll mill at 190°C and 15/20 rpm. The test was stopped when the rolling hide became brown in color.

Test product	Tack-free time	Final stability
Copolymer I (according to Example 1)	27 min	30 min
Copolymer II (according to Example 2)	30 min	30 min
Copolymer III (according to Example 3)	22 min	35 min
Ethylene glycol montanate (Hoechst Wachs E)	16 min	35 min

Example 6

A PVC compound having the following composition

S-PVC, K value about 58	100.0 parts by weight
Liquid zinc stabilizer	0.1 part by weight
Calcium stearate	0.3 part by weight
Costabilizer (β-diketone)	0.3 part by weight
Epoxidized soybean oil (ESO)	3.0 parts by weight
MBS impact modifier	8.0 parts by weight
Processing auxiliary containing acrylate	1.0 part by weight
Glycerol monooleate	1.0 part by weight
Brightening agent (blue pigment)	2.0 parts by weight
Test product	1.2 parts by weight

was milled on a roll mill at 190°C for 5 minutes. Samples of the hide were then taken and tested for their yellowness index (YI) with a colorimeter.

Test product	YI
Copolymer I (according to Example 1)	-31.8
Copolymer II (according to Example 2)	-31.4
Copolymer III (according to Example 3)	-29.0
Ethylene glycol montanate (Hoechst Wachs E)	- 27.2

Example 7

A PVC compound having the composition

E-PVC (K value about 78)	100.0 parts by weight
Diphenylthiourea	0.5 part by weight
Test product	3.0 parts by weight

was milled on a roll mill at 190°C and 15/20 rpm. The time taken for complete formation of a homogeneous rolling hide (hide formation time) was determined.

Test product	Hide formation time (minutes)
Copolymer I (according to Example 1)	1.0
Copolymer II (according to Example 2)	1.0
Ethylene glycol montanate (Hoechst Wachs E)	4.0

~~Patent Claims~~ HOE 91/F 369

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A copolymer comprising
20 to 99.5 parts by weight of units which are derived from a C_{12}-C_{60}-α-olefin,
0.5 to 50 parts by weight of units which are derived from a carboxylic acid of the formula $CH_2=CR^1-COOH$,
0.1 to 60 parts by weight of units which are derived from a carboxylic acid ester of the formula $CH_2=CR^1-COOR^2$, in which formulae R^1 is a hydrogen atom or a methyl group and R^2 is a straight-chain or branched alkyl radical havingh 1 to 6 carbon atoms, and
0.0 to 30 parts by weight of units which are derived from styrene, 3-methylstyrene, 4-methylstyrene or α-methylstyrene.

2. A copolymer as claimed in claim 1, in which the α-olefin is a C_{18} to C_{60}-α-olefin.

3. A copolymer as claimed in claim 1, in which the α-olefin is a C_{24} to C_{60}-α-olefin.

4. A copolymer as claimed in claim 1, in which the carboxylic acid ester of the formula $CH_2=CR^1-COOR^2$ is an ester in the formula of which R^1 is a hydrogen atom or a methyl group and R^2 is a methyl or ethyl group.

5. The use of a copolymer as claimed in claim 1 as a processing auxiliary for thermoplastics.

6. A thermoplastic molding composition comprising 0.05 to 5% by weight, based on the molding composition, of a copolymer as claimed in claim 1.

7. A thermoplastic molding composition as claimed in claim 6, which is based on polyvinyl chloride,

polyvinylidene chloride, an ethylene/vinyl acetate copolymer, polyacrylonitrile, a graft polymer or copolymer of vinyl chloride and vinyl acetate or a mixture of these thermoplastics.

8. A thermoplastic molding composition as claimed in claim 6 which additionally comprises fillers, heat stabilizers, light stabilizers, antistatics, flame-proofing agents, reinforcing substances, pigments, dyestuffs, processing auxiliaries, lubricants, impact modifiers, antioxidants, blowing agents or optical brighteners.

DATED this 26th day of November 1992.

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Abstract of the disclosure: HOE 91/F 369

Copolymers and their use as lubricants and release agents for processing thermoplastics

Copolymers prepared by free radical polymerization of a C_{12}-C_{60}-α-olefin with a carboxylic acid of the formula $CH_2=CR^1-COOH$, a carboxylic acid ester of the formula $CH_2=CR^1-COOR^2$ and, if appropriate, a styrene compound prove to be highly active lubricants and release agents in polymers, in particular in polyvinyl chloride, which scarcely influence the transparency of the polymers.