

5 The invention relates to a process for the preparation of linear alternating copolymers of carbon monoxide with one or more compounds comprising an ethylenically unsaturated bond, to compositions containing the copolymers and to a method for melt processing the copolymers.

10 It is known that linear copolymers in which the units originating from carbon monoxide substantially alternate with the units originating from the ethylenically unsaturated compound(s), may be prepared by contacting the monomers under polymerization conditions in the presence of a suitable catalyst.

15 Convenient methods for preparing such copolymers are disclosed in, inter alia, EP-A-181014 and EP-A-248483. The copolymers obtained according to these, or similar preparation methods, are relatively high molecular weight compounds, having established utility as thermoplastics in the production of shaped articles, such as containers for foods and drinks and parts for the car industry and for various applications in the domestic sphere.

20 For these uses and the like, the copolymers have to be melt processed, i.e. they have to be brought in molten state so that they can be moulded or extruded. In view of their high melting point, usually of 200 °C or even higher, the melt stability of the copolymers may become a problem if the copolymers are to remain in molten state for a substantial length of time. The longer the copolymers are subjected to high temperatures, the more they are susceptible to degradation caused by chemical reactions.

25 The formation of degradation products will usually be at the expense of the properties of the copolymer product.

30 The presence of specific impurities in the copolymers may have a negative effect on the stability of the copolymers whilst being processed at high temperatures.

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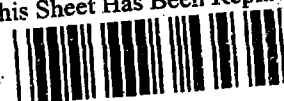
5 It has already been proposed to reduce the content of typical
impurities, such as sulphur in sulphidic form and iron present as
iron carbonyl, which impurities often occur in the carbon monoxide
feedstock, in particular if the carbon monoxide used is a
commercial grade feedstock, such as commonly available at
10 (petro)chemical sites. Whilst a reduction in the content of these
impurities in the carbon monoxide monomer feed has a favourable
effect on the average reaction rate at which the polymerization
proceeds, it has little effect on the melt stability of the
copolymers obtained.

15 It has now been found that the melt stability of the
copolymers of the invention is adversely affected by the presence
therein of trace quantities of alkali(ne earth) metal salt
impurities. It has also been found that a significant improvement
in melt stability is achieved by reducing the alkali(ne earth)
20 metal salt content of the produced copolymers or by adding to a
copolymer which is contaminated with alkali(ne earth) metal salt a
substance which is able to bind the contaminating salt. Evidently,
both treatments may be combined as well.

25 The detrimental influence of minute quantities of alkali(ne
earth) metal salts on the melt stability of the copolymers is
surprising in view of the prior art. For example, in EP-A-285218 it
is proposed to treat the copolymers with alkali metal
N,N-diethyldithiocarbamate as a step in reducing the concentration
of palladium or nickel catalyst remnants for the purpose of
30 improving the copolymers' melt stability. In US-A-3948850 it is
proposed to stabilise ethylene/carbon monoxide copolymers having up
to 50 %mol carbon monoxide by adding thereto a dihydro phosphoric
acid salt of an alkali(ne earth) metal.

35 Calcium hydroxyapatite and zeolites containing a metal of
Group 2 of the Periodic Table, such as calcium, have been

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5 alkali(ne earth) metal salts which may be present in the polymers
need to be removed or need to be bound in order to stabilize the
copolymers, as opposed to the prior art which teaches that these
metals have to be added. With hindsight it is conceivable that the
10 stabilization achieved by the addition of calcium hydroxyapatite or
a Group 2 metal containing zeolite may (in part) have been the
result of interaction of the apatite or the zeolite with any
alkali(ne earth) metal salt present in the polymer. However, from
the documents nothing can be learnt in that respect and since there
is no mention of removal of stabilisers from the copolymers, a
15 reduction of the alkali(ne earth) metal salt content thereof has
not been effected. For completeness' sake it is noted that in
GB-A-2249549 there is a single mention of a destabilizing effect of
sodium and potassium containing zeolite when added to the copolymer
in quantities which, however, exceed by far the trace level.

20 Accordingly, the invention relates to a process for the
preparation of linear alternating copolymers of carbon monoxide and
one or more ethylenically unsaturated compounds by reacting the
monomers under polymerization conditions in the presence of a
suitable catalyst system, one or more components present in the
25 reaction mixture being contaminated with alkali(ne earth) metal
salt(s), which process involves a treatment by which at least part
of the alkali(ne earth) metal salt is removed such that the total
amount of alkali(ne earth) metals present in the copolymerization
product is less than 1 part per million by weight.

30 The invention also relates to a copolymer composition
comprising a linear alternating copolymer of carbon monoxide and
one or more ethylenically unsaturated compounds, a contaminant
comprising an alkali(ne earth) metal salt and a stabilizing
quantity of a substance which is able to bind at least part of the

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5 one or more ethylenically unsaturated compounds, wherein a linear
alternating copolymer of carbon monoxide and one or more
ethylenically unsaturated compounds which contains a contaminant
comprising an alkali(ne earth) metal salt is mixed with a
10 stabilizing quantity of a substance which is able to bind at least
part of the alkali(ne earth) metal salt, the substance being other
than a hydroxyapatite or a zeolite-type trivalent metal silicate,
and wherein the resulting mixture is melt processed.

As the alkali(ne earth) metal contaminants are present in the
form of salts, for example sodium chloride, sodium acetate or
15 sodium silicate, the treatment according to this invention effects,
in addition to a reduction of the alkali(ne earth) metal content,
also a reduction of the content of the accompanying anion of the
copolymerization product.

Depending on the origin of the alkali(ne earth) metal salt
20 impurities, the treatment resulting in a decrease in alkali(ne
earth) metal content of the copolymers produced, may be carried out
after, during or prior to the copolymerization reaction. For
example, in the event that the impurities are introduced into the
reactor, as contaminants in more than one of the reactor
25 components, the treatment will preferably be carried out during the
polymerization reaction.

In the event that the source of alkali(ne earth) metal salt
impurities can be attributed to a specific component in the
reaction mixture, it is advantageous to subject only that component
30 to the said treatment, prior to its use in the polymerization
reaction. For example, if the copolymerization is carried out in
the presence of a diluent which is contaminated with alkali(ne
earth) metal salts, it is preferred to reduce the alkali(ne earth)
metal salt content of the diluent before introducing the diluent
35 into the reactor. Thus, when said treatment is carried out during

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5 is reduced.

It has been observed that the alkali(ne earth) metal content of the copolymers, produced by a process not involving the treatment according to the invention, is usually in the range of 1-5 parts per million by weight (ppmw). Conceivably in some cases the alkali(ne earth) metal content may be up to 100 ppmw. The melt stability of these copolymers is usually unsatisfactory. The treatment of the invention results in a substantial improvement in melt stability of the copolymers and is performed such that the alkali(ne earth) metal content of the copolymers is reduced to less than 1 ppmw and preferably to less than 0.1 ppmw. When said treatment is carried out during or prior to the copolymerization the alkali(ne earth) metal salt(s) is/are preferably removed to such an extent that the alkali(ne earth) metal content of the reaction mixture is below 0.5 ppmw and more preferably below 0.05 ppmw.

For the removal of alkali(ne earth) metal salt(s) various treating methods may be elected. A convenient method may consist in contacting the reaction mixture, or one or more components thereof, such as a contaminated starting material or a contaminated diluent, with a solid material capable of binding or otherwise inactivating the contaminating alkali(ne earth) metal salts, followed by at least partly removal of the alkali(ne earth) metal-enriched solid material.

For example, if a liquid diluent or solvent is used which is contaminated with alkali metal salts, it is recommended to pass the impure liquid through a bed, substantially consisting of solid adsorbent, followed by passing the purified liquid to the reactor. Alternatively, finely divided solid adsorbent particles may be admixed with the contaminated liquid, followed by filtering off the

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5 propene, may be carried out in a similar manner. In principle the alkali(ne earth) metal-enriched adsorbent, when formed during or after the polymerization process, is separated from the copolymers, e.g. by selectively dissolving the latter and removing the alkali(ne earth) metal-enriched adsorbent from the solution.

10 However, only a few solvents are capable of selectively dissolving the copolymers. Therefore it is preferred that a treatment comprising the use of a solid adsorbent is carried out at a stage before the copolymers are formed.

15 Preferred adsorbents are solid materials, capable of adsorbing, generally as a heterogeneous adsorbent, a major part of the alkali(ne earth) metal ions, such as sodium, lithium and potassium ions, and a major part of the accompanying anions, such as chloride, bromide and acetate ions. Suitable are e.g. ion-exchange resins, zeolites and basic solid materials.

20 A good adsorbent for the treatment of the invention are apatites, having the general formula $M_{10}(PO_4)_6X_nY_{2-n}$, wherein M is barium, strontium or, preferably, calcium, n is 0, 1 or 2, X is OH and Y is fluorine. Calcium hydroxyapatite is a naturally occurring calcium phosphate, being the major constituent of bone and tooth
25 mineral. It is a crystalline, material, also referred to as tribasic calcium phosphate. However, when the treatment of this invention involves treating a lower aliphatic alcohol, for example methanol, or a mixture containing a substantial quantity of a lower aliphatic alcohol it is less preferred to use an apatite as the
30 adsorbent because, as is known in the art, apatites may not be completely inert in lower aliphatic alcohols.

Suitable ion exchange resins are typically resins containing strong acidic groups, such as sulphonic acid groups, as the cation exchanging groups on a matrix. For the exchange of anions
35 accompanying the alkali(ne earth) metal a strong basic ion exchange

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5 cation exchanging groups on a single matrix. Cross-linked
polystyrene is a suitable matrix for ion exchange resins, other
matrices being suitable as well. Very suitable systems of one or
more ion exchange resins are those which can be used in water
10 demineralisation processes. Very good results have been obtained
with a mixed bed ion exchange resin.

Although the amount of solid adsorbent is not critical,
usually a limited amount is used, in order to avoid the handling
and removal of large amounts of material. Preferably the amount of
solid adsorbent is less than 5% by weight of the treated
15 contaminated component(s) of the reaction mixture. Most preferably
the amount of solid adsorbent is selected in the range of 0.000001
to 0.5% by weight of the component(s) to be treated.

It may be convenient to use the electrical conductivity as a
characterization of liquid components, which are usually
20 essentially organic and non-ionic by nature, after they have been
treated with an adsorbent. Suitably the electrical conductivity is
lower than 200 $\mu\text{S/m}$, preferably less than 100 $\mu\text{S/m}$ and in
particular less than 60 $\mu\text{S/m}$. Throughout this application the
electrical conductivities are specified as conductivities measured
25 at 20 °C.

A treatment according to this invention which does not involve
the use of a solid adsorbent may comprise washing the copolymer
powder as prepared in the reactor with a washing liquid which is
able to remove alkali(ne earth) metal salts from the copolymer. The
30 invention also relates to a washing per se comprising washing a
preformed reactor powder of the copolymer which contains a
contaminant comprising an alkali(ne earth) metal salt with a
washing liquid which is able to remove at least part of the
alkali(ne earth) metal salt(s) from the copolymer, preferably such

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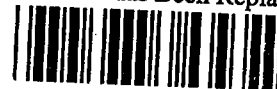


5 substantially free of alkali(ne earth) metal salts, for example by
being prior treated with one or more ion exchange resins as
described hereinbefore. The washing liquid is suitably essentially
organic, polar and non-ionic by nature, for example an aliphatic
alcohol or ketone having up to four carbon atoms, and has typically
10 an electrical conductivity of less than 200 $\mu\text{S/m}$. It may be
advantageous to have water present in such a washing liquid, for
example 1 - 20 %vol relative to the resultant liquid mixture, with
an equal content of alkali(ne earth) metal(s), relative to the
total weight of the liquid. The washing liquid may also essentially
15 consisting of water having an electrical conductivity of less than
1000 $\mu\text{S/m}$, in particular less than 600 $\mu\text{S/m}$. Very good results can
be obtained by washing a copolymer powder, contaminated with
alkali(ne earth) metal salt, with methanol or with methanol/water
(95/5 v/v) which has prior been made essentially free of alkali(ne
20 earth) metal salt by a treatment with one or more ion exchange
resins.

Another example of a suitable washing liquid may be a diluent
in which the copolymer is insoluble or virtually insoluble and to
which one or more complexing agents for the contaminating alkali(ne
25 earth) metal ion(s) have been added, such as crown ethers.

The catalyst system used in the process of the invention is
preferably a catalyst containing one or more metals of Group VIII
of the Periodic Table. The amount of such a catalyst is not
critical and may vary within wide ranges, e.g. between 10^{-7} and
30 10^{-2} gram atom of Group VIII metal per mol of ethylenically
unsaturated compound to be copolymerized. Preferably the amount is
between 10^{-6} and 10^{-4} on the same basis. With a view at their
thermal stability copolymers are typically prepared which contain
less than 20 ppmw Group VIII metal, preferably less than 10 ppmw
35 and in particular less than 5 ppmw.

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5 preferred.

Very suitable catalyst systems are catalytically active compositions based on a palladium compound, an anion of an acid with a pKa of less than 6, preferably less than 4, and a bidentate ligand.

10 Preferred bidentate ligands may be indicated by the general formula $R^1R^2M^1-R-M^2R^3R^4$ wherein each of M^1 and M^2 independently represents a phosphorus, arsenic, antimony or nitrogen atom, each of R^1 , R^2 , R^3 and R^4 independently represents a substituted or non-substituted hydrocarbyl group and R represents a divalent
15 organic bridging group containing at least two carbon atoms in the bridge.

Preferably M^1 and M^2 each represent a phosphorus atom. Suitably R^1 , R^2 , R^3 and R^4 represent the same, optionally substituted hydrocarbyl group, preferably an aromatic group such as
20 phenyl, diphenyl or naphthyl group or an aromatic group containing one or more substituents, in particular polar substituents such as halogen atoms, halogenated alkyl groups, alkoxy groups such as methoxy, ethoxy or isopropoxy groups, hydroxyl, (di)alkylamino or ester groups.

25 Preferably one or two substituents are located at the ortho position(s) in the aromatic ring with respect to the phosphorus atom to which that aromatic group is linked.

The copolymerization process of the invention may proceed in the gasphase, but is typically carried out by contacting the
30 monomers in the presence of a suitable diluent with the catalyst system, usually a solution of a compound of a Group VIII metal in a suitable solvent, such as a lower ketone or a lower aliphatic alcohol, for example acetone or methanol. Suitable diluents are typically those in which the formed copolymers are insoluble or
35 virtually insoluble. The diluent is preferably a protic compound,

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5 Ethylenically unsaturated compounds suitable to be
copolymerized with carbon monoxide in the process of the invention
include compounds consisting exclusively of carbon and hydrogen and
compounds which in addition contain one or more heteroatoms,
typical examples being unsaturated esters such as methyl acrylate.
10 Preferably, however, unsaturated hydrocarbons are used, in
particular lower olefins such as ethene, propene and butene-1 and
mixtures thereof and olefins substituted by an aromatic group such
as styrene and p-alkylstyrenes. Ethene and mixtures comprising
ethene and propene are in particular preferred starting materials.
15 The molar ratio between the monomers, viz. carbon monoxide and the
ethylenically unsaturated compound(s), is suitably selected in the
range of 5:1 to 1:5, preferably in the range of 1.5:1 to 1:1.5.

 The copolymerization reaction is suitably carried out at a
temperature in the range of 10-200 °C and a pressure in the range
20 of 1 to 200 bar. Preferred temperatures are in the range of
20-180 °C, in particular in the range of 30-150 °C. Preferred
pressures are selected in the range of 5 to 100 bar.

 In other embodiments of this invention the stability of a
linear alternating copolymer of carbon monoxide and one or more
25 ethylenically unsaturated compounds which is contaminated with an
alkali(ne earth) metal salt is improved by using as a stabiliser a
substance which is able to bind at least a part of the alkali(ne
earth) metal salt. As discussed hereinbefore, the use of a
stabilizing quantity of a hydroxyapatite or a zeolite-type
30 trivalent metal silicate in these polymers, conceivably effecting
the binding of alkali(ne earth) metal salts in the copolymers, is
known in the art and is excluded from the protection of these
embodiments of the invention.

 The alkali(ne earth) metal salt binding substances used in the
35 compositions of the invention and in the method of melt processing

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5 zirconium phosphates, such as alpha- and gamma-zirconium phosphate,
and lanthanum phosphate. Good stabilizing activities have been
found when using one or more of barium phosphate, lanthanum
phosphate, magnesium orthophosphate, calcium silicium phosphate,
magnesium silicium phosphate, aluminium phosphate and fluorapatite
10 (i.e. a mineral of the formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$). Preferred stabilisers
are selected from the group consisting of lanthanum phosphate,
magnesium silicium phosphate and calcium silicium phosphate.

The quantity of the alkali(ne earth) metal salt binding
substances to be used is not critical as long as melt stabilization
15 of the copolymer is effected. Usually a quantity in the range of
from 0.01 %w to 5.0 %w, relative to the quantity of the copolymer,
will be effective, in particular from 0.02 %w to 1.0 %w and more in
particular from 0.05 %w to 0.5 w%, on the same basis.

These substances are frequently solids thus forming a solid
20 phase in the compositions of the invention. They are preferably
used as a finely divided material, typically having a
volume-average particle size in the range of 0.1 - 50 μm , in
particular in the range of 0.5 - 10 μm .

The melt stability of the copolymers may be further improved
25 by adding one or more (further) stabilizers, conveniently by dry
blending of the copolymers and the stabilizing compounds, at any
downstream stage of the process. Materials known to be suitable in
this respect, include inorganic or organometallic compounds, such
as zinc aluminates, alumina hydrogels and cupric chromite. As
30 mentioned hereinbefore, calcium hydroxyapatite and calcium
containing zeolites have also been recommended as a suitable
stabilizer. Also other additives may be included in the
compositions, such as antioxidants, dyes, fillers or reinforcing
agents, fire resistant materials, mould release agents, colorants

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5 sheets, plates and shaped articles.

The invention is illustrated by the following non-limiting experiments and examples.

Experiment 1

10 The influence of trace quantities of various salts on the melt stability of a linear alternating copolymer of carbon monoxide, ethene and propene was measured as follows.

15 Samples of the linear alternating copolymer of carbon monoxide, ethene and propene (melting point 222 °C) were loaded with any one of the salts, as indicated in Table I, by impregnating the samples with a solution of the salt in de-ionized (double-distilled) water and drying. For comparison one copolymer sample was treated in the same way with de-ionized water, but without a salt dissolved therein. The resultant copolymer powders were compression moulded to form 1 mm thick sheets by pressing at 250 °C
20 for 0.5 minutes at 4 kg/cm² and 1.5 minutes at 40 kg/cm². Circular discs cut from the sheets were subjected to dynamic rheology testing, i.e. measurement of dynamic shear moduli, at a temperature of 275 °C, using an angular frequency of 1 rad/s and the sample being hold between aluminium discs at a distance of 0.9 mm. The
25 aluminium discs were disposable discs, pretreated with an Alodine S solution. The cross-over time (COT), which is defined as the time elapsed since sample loading until the loss factor (i.e. the ratio of the loss modulus G'' and the storage modulus G') equals 1, is indicated in Table I for each sample. A higher cross-over time is
30 indicative for a better thermal stability of the copolymer.

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	-	32
5	Sodium chloride (5.0)	10
	Sodium bromide (5.0)	11
	Sodium iodide (5.0)	13
	Sodium acetate (5.0)	7
	Sodium nitrate (5.0)	12
10	Sodium sulphate (5.0)	23
	Sodium perchlorate (5.0)	5
	Potassium bromide (8.6)	8
	Magnesium sulphate (5.3)	15
	Calcium chloride (8.2)	1
15	Barium bromide (30.2)	2

These experiments show that trace amounts of alkali(ne earth) metal salts contaminating the linear alternating copolymers have a detrimental influence on the copolymers' melt stability.

Experiment 2

20 The thermal stability of a model compound, representing a carbon monoxide/ethene copolymer, and the influence of (the removal of) trace quantities of alkali(ne earth) metal impurities thereon were measured as follows. The model compound, tetradecan-3,6,9,12-tetraone, was prepared by using methods described by H. Stetter, 25 Angew. Chem. 88 (1976) pp. 695 ff.

Tetradecan-3,6,9,12-tetraone (1 g, containing 300 ppmw sodium) was dissolved in 50 ml dichloromethane which was essentially free of alkali(ne earth) metal. Calcium hydroxyapatite (0.04 g, containing less than 0.1 %w sodium) was suspended in this solution. 30 The resulting suspension was stirred for 1 hour and filtered. The tetradecan-3,6,9,12-tetraone was recovered by evaporating the

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5 Samples of the fresh and of the recovered tetradecan-3,6,9,12-
tetraone were heated at 240 °C under nitrogen. GLC analysis carried
out after 24 hours of heat exposure revealed that the untreated
tetradecan-3,6,9,12-tetraone was completely converted (degraded)
and that 94 % of the recovered tetradecan-3,6,9,12-tetraone was
10 converted into a range of decomposition products.

The above experiment was repeated using 1 g of a different
sample of the tetradecan-3,6,9,12-tetraone and using 0.04 g
lanthanum phosphate instead of calcium hydroxyapatite.

15 Elemental analyses of the fresh and the recovered tetradecan-
3,6,9,12-tetraone were as follows: 9 ppmw and 2 ppmw sodium,
3.5 ppmw and 0.6 ppmw calcium, 0.2 ppmw and 0.2 ppmw magnesium,
less than 0.5 ppmw and 35 ppmw lanthanum, respectively. The
elemental analyses of the fresh and the recovered lanthanum
phosphate were as follows: 55 ppmw and 500 ppmw sodium, 45 ppmw and
20 180 ppmw calcium, less than 30 ppmw and 70 ppmw magnesium,
respectively.

GLC analyses after heating the fresh and the recovered tetra-
decan-3,6,9,12-tetraone (240 °C, 20 hours) revealed that the 60 %
of the fresh model compound was converted and 20 % of the recovered
1 25 model compound.

These experiments show that calcium hydroxyapatite and
lanthanum phosphate adsorb alkali(ne earth) metal contaminants and
that the treatment of the model compound with calcium
hydroxyapatite or lanthanum phosphate leads to an improvement in
30 thermal stability. There is also a correlation between the rate of
decomposition upon heating at 240 °C and the alkali(ne earth) metal
content of the tested samples. It is evident that the melt
stability of linear alternating copolymers of carbon monoxide and
ethylenically unsaturated compounds can be improved by removing

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5 4000ml autoclave equipped with a stirrer was charged with 1500 ml
methanol/water (95/5 v/v) containing alkali metal salt contaminants
and having an electrical conductivity of 360 $\mu\text{S/m}$. The reactor was
closed and the air therein was removed by pressurising with carbon
monoxide to 15 bar and releasing the pressure. This procedure of
10 pressurising and pressure release was repeated three times. The
temperature in the autoclave was raised to 88 °C and a mixture of
carbon monoxide and ethene in a 2:1 ratio was introduced until the
pressure was 26 bar. A catalyst solution containing 0.0065 mmol
15 palladium acetate, 0.0069 mmol 1,3-bis[bis(2-methoxyphenyl)-
phosphinolpropane, 0.0040 mmol trifluoroacetic acid and 4.3 ml
acetone was added. The acetone used for preparing the catalyst
solution contained alkali metal salt contaminants and had an
electrical conductivity of 75 $\mu\text{S/m}$.

20 After a period of 17 hours the polymerisation was terminated
by cooling the reaction mixture to room temperature and releasing
the pressure. Solid powdery product was filtered off, washed with
methanol/water, which was taken from the same stock as the diluent
used in the polymerization, and dried.

25 A sample of the obtained white polymer powder was compression
moulded using substantially the procedure as described in
Experiment 1. The sheet obtained was whitish with a grizzly shade.

Example 2

A carbon monoxide/ethene polymer was prepared substantially as
30 described in Example 1, but with the differences that prior to
their use in the preparation the methanol/water and the acetone
were both percolated over a mixed bed anion/cation exchange resin
purchased under the trade name MILLIPORE ION-EX CARTRIDGE. The
electrical conductivities of the percolated methanol/water and
35 acetone were 57 $\mu\text{S/m}$ and 38 $\mu\text{S/m}$, respectively.

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5 with the colour of the sheet obtained in Example 1 is indicative for an improved thermal stability of the copolymer.

Example 3

10 A carbon monoxide/ethene polymer was prepared substantially as described in Example 1. A sample of the copolymer powder obtained was washed four times with methanol which methanol was prior percolated over a mixed bed anion/cation exchange resin purchased under the trade name MILLIPORE ION-EX CARTRIDGE. The electrical conductivity of the percolated methanol was 23 $\mu\text{S/m}$.

15 The washed copolymer powder was compression moulded and tested in dynamic rheology testing substantially as described in Experiment 1. The cross-over time was 20 minutes.

20 The electrical conductivities of the washing liquids obtained in each washing were 650 $\mu\text{S/m}$, 200 $\mu\text{S/m}$, 60 $\mu\text{S/m}$ and 52 $\mu\text{S/m}$, respectively, indicating that alkali metal salt impurities were removed from the copolymer in each of the washings.

For comparison a sheet was compression moulded from a sample of the un-washed copolymer and a circular disc cut from the sheet was subjected to the dynamic rheology testing. The cross-over time was 14 minutes.

25 The improved thermal stability of the washed sample is evident from a comparison of the cross-over times.

Examples 4 - 13

30 Samples of a linear alternating copolymer of carbon monoxide, ethene and propene (melting point 222 °C), which was contaminated with alkali metal salt, were powder blended with 0.25 %w or 0.20 %w (calculated on the weight of the composition) of any one of the phosphates indicated in Table II. The resultant powder mixtures were compression moulded and tested in dynamic rheology testing substantially as described in Experiment 1. For comparison a sample

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Example	Phosphate (concentration, %w)	COT minutes
4	- *)	22
5	Calcium hydroxyapatite (0.25) *)	39
6	Lanthanum phosphate (0.25)	39
7	Barium phosphate (0.25)	33
10	8 Calcium fluorapatite (0.25)	28
	9 Magnesium orthophosphate (0.20)	37
	10 Calcium phosphate (0.20)	31
	11 Calcium silicium phosphate (0.20)	39
	12 Magnesium silicium phosphate (0.20)	30
15	13 Aluminium phosphate (0.20)	29

*) for comparison, not according to invention

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1. A process for the preparation of linear alternating copolymers of carbon monoxide and one or more ethylenically unsaturated compounds by reacting the monomers under polymerization conditions in the presence of a suitable catalyst system, one or more
5 components present in the reaction mixture being contaminated with alkali(ne earth) metal salt(s), which process involves a treatment by which at least part of the alkali(ne earth) metal salt is removed such that the total amount of alkali(ne earth) metals present in the copolymerization product is less than 1 part per
10 million by weight.
2. A process as claimed in claim 1, characterized in that the total amount of alkali(ne earth) metals is less than 0.1 part per million by weight.
3. A process as claimed in claim 1 or 2, characterized in that
15 said treatment is carried out during or prior to the copolymerization reaction and comprises treating one or more alkali(ne earth) metal(s) containing components of the reaction mixture before being introduced into the copolymerization reactor.
4. A process as claimed in claim 3, characterized in that the
20 said treatment consists in contacting one or more of the components of the reaction mixture with a solid adsorbent, capable of adsorbing ions of alkali(ne earth) metal salts, followed by at least partly removal of alkali(ne earth) metal-enriched adsorbent.
5. A process as claimed in claim 4, characterized in that the
25 solid adsorbent comprises one or more ion exchange resins containing anion exchanging and cation exchanging groups on a matrix, optionally combined on a single matrix.
6. A process as claimed in claim 4 or 5, characterized in that
30 the amount of solid adsorbent is in the range of 0.000001 to 0.5% by weight of the component(s) treated.

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- 5 insoluble or virtually insoluble and which has an electrical
conductivity of less than 200 $\mu\text{S/m}$.
8. A process as claimed in any of claims 1 - 7, characterized in
that the catalyst system contains at least one metal of Group VIII
of the Periodic Table and is used in an amount such that per mol of
10 ethylenically unsaturated compound to be copolymerized it contains
 10^{-6} - 10^{-4} gram atom of Group VIII metal.
9. A process as claimed in claim 8, characterized in that a
catalyst system is used which is based on palladium as Group VIII
metal, an anion of an acid with a pKa of less than 4 and a
15 bidentate ligand of the general formula $\text{R}^1\text{R}^2\text{M}^1\text{-R-M}^2\text{R}^3\text{R}^4$ wherein
each of M^1 and M^2 independently represents a phosphorus, arsenic,
antimony or nitrogen atom, each of R^1 , R^2 , R^3 and R^4 independently
represents a substituted or non-substituted hydrocarbyl group and R
represents a divalent organic bridging group containing at least
20 two carbon atoms in the bridge.
10. A process as claimed in claim 9, characterized in that a
catalyst system is used comprising a bidentate ligand of the
general formula $\text{R}^1\text{R}^2\text{P-R-PR}^3\text{R}^4$ wherein at least one of R^1 , R^2 , R^3
and R^4 represents an aromatic group substituted by a polar group,
25 in particular an alkoxy group, at one or both ortho positions with
respect to the phosphorus atom to which the aromatic group is
linked.
11. A process as claimed in any of claims 1 - 10, characterized in
that as ethylenically unsaturated compound ethene or a mixture of
30 ethene and propene is used, in that the molar ratio between carbon
monoxide on the one hand and the ethylenically unsaturated
compound(s) on the other, is in the range from 5:1 to 1:5, in
particular in the range from 1.5:1 to 1:1.5, and in that the
reaction is carried out in the presence of a protic diluent, for

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- 5 ethylenically unsaturated compounds comprising washing a preformed reactor powder of the copolymer which contains a contaminant comprising an alkali(ne earth) metal salt with a washing liquid which is able to remove at least part of the alkali(ne earth) metal salt(s) from the copolymer.
- 10 13. A copolymer composition comprising a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds, a contaminant comprising an alkali(ne earth) metal salt and a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the
- 15 substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate.
14. A copolymer composition as claimed in claim 13, characterized in that the substance which is able to bind at least part of the alkali(ne earth) metal salt is selected from the group consisting
- 20 of barium phosphate, lanthanum phosphate, magnesium orthophosphate, calcium silicium phosphate, magnesium silicium phosphate, aluminium phosphate and fluorapatite.
15. A copolymer composition as claimed in claim 14, characterized in that the substance which is able to bind at least part of the
- 25 alkali(ne earth) metal salt is selected from the group consisting of lanthanum phosphate, magnesium silicium phosphate and calcium silicium phosphate.
16. A copolymer composition as claimed in any of claims 13 - 15, characterized in that the substance which is able to bind at least
- 30 part of the alkali(ne earth) metal salt is used in a quantity of in the range of from 0.02 %w to 1.0 w%, relative to the quantity of the copolymer.
17. A copolymer composition as claimed in claim 16, characterized in that the substance which is able to bind at least part of the
- 35 alkali(ne earth) metal salt is used in a quantity of in the range

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5 compounds, wherein a linear alternating copolymer of carbon
monoxide and one or more ethylenically unsaturated compounds which
contains a contaminant comprising an alkali(ne earth) metal salt is
mixed with a stabilizing quantity of a substance which is able to
bind at least part of the alkali(ne earth) metal salt, the
10 substance being other than a hydroxyapatite or a zeolite-type
trivalent metal silicate, and wherein the resulting mixture is melt
processed, such as by extrusion or injection moulding.

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PREPARATION OF COPOLYMERS OF CARBON MONOXIDE WITH ETHYLENICALLY
UNSATURATED COMPOUNDS, COMPOSITION AND METHOD FOR MELT PROCESSING

A process for the preparation of linear alternating copolymers of carbon monoxide and an ethylenically unsaturated compound by polymerizing the monomers in the presence of a suitable catalyst system, one or more components present in the reaction mixture being contaminated with alkali(ne earth) metal salt(s), which process involves a treatment by which at least part of the alkali(ne earth) metal salt is removed such that the total amount of alkali(ne earth) metals present in the copolymerization product is less than 1 part per million by weight; a copolymer composition comprising said copolymer, an alkali(ne earth) metal salt contaminant and a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate; and a method for melt processing said copolymer, wherein the copolymer which contains an alkali(ne earth) metal salt contaminant is mixed with a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate, and wherein the resulting mixture is melt processed.

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The invention relates to a process for the preparation of linear alternating copolymers of carbon monoxide with one or more compounds comprising an ethylenically unsaturated bond, to compositions containing the copolymers and to a method for melt processing the copolymers.

It is known that linear copolymers in which the units originating from carbon monoxide substantially alternate with the units originating from the ethylenically unsaturated compound(s), may be prepared by contacting the monomers under polymerization conditions in the presence of a suitable catalyst.

Convenient methods for preparing such copolymers are disclosed in, inter alia, EP-A-181014 and EP-A-248483. The copolymers obtained according to these, or similar preparation methods, are relatively high molecular weight compounds, having established utility as thermoplastics in the production of shaped articles, such as containers for foods and drinks and parts for the car industry and for various applications in the domestic sphere.

For these uses and the like, the copolymers have to be melt processed, i.e. they have to be brought in molten state so that they can be moulded or extruded. In view of their high melting point, usually of 200 °C or even higher, the melt stability of the copolymers may become a problem if the copolymers are to remain in molten state for a substantial length of time. The longer the copolymers are subjected to high temperatures, the more

product.

The presence of specific impurities in the copolymers may have a negative effect on the stability of the copolymers whilst being processed at high temperatures.

The origin of these impurities is not always known, but in many cases they are apparently introduced in the reactor, together with the starting materials, the catalyst or with the diluent or solvent, if any.

It has already been proposed to reduce the content of typical impurities, such as sulphur in sulphidic form and iron present as iron carbonyl, which impurities often occur in the carbon monoxide feedstock, in particular if the carbon monoxide used is a commercial grade feedstock, such as commonly available at (petro)chemical sites. Whilst a reduction in the content of these impurities in the carbon monoxide monomer feed has a favourable effect on the average reaction rate at which the polymerization proceeds, it has little effect on the melt stability of the copolymers obtained.

It has now been found that the melt stability of the copolymers of the invention is adversely affected by the presence therein of trace quantities of alkali(ne earth) metal salt impurities. It has also been found that a significant improvement in melt stability is achieved by reducing the alkali(ne earth) metal salt content of the produced copolymers or by adding to a copolymer which is contaminated with alkali(ne earth) metal salt a substance which is able to bind the contaminating salt. Evidently, both treatments may be combined as well.

The detrimental influence of minute quantities of

as a step in reducing the concentration of palladium or nickel catalyst remnants for the purpose of improving the copolymers' melt stability. In US-A-3948850 it is proposed to stabilise ethylene/carbon monoxide copolymers having up to 50 %mol carbon monoxide by adding thereto a dihydro phosphoric acid salt of an alkali(ne earth) metal.

Calcium hydroxyapatite and zeolites containing a metal of Group 2 of the Periodic Table, such as calcium, have been recommended as melt stabilizers for the linear alternating copolymers of carbon monoxide and ethylenically unsaturated compounds (cf. EP-A-478088 and GB-A-2249549, respectively). The present invention surprisingly teaches that trace quantities of the alkali(ne earth) metal salts which may be present in the polymers need to be removed or need to be bound in order to stabilize the copolymers, as opposed to the prior art which teaches that these metals have to be added. With hindsight it is conceivable that the stabilization achieved by the addition of calcium hydroxyapatite or a Group 2 metal containing zeolite may (in part) have been the result of interaction of the apatite or the zeolite with any alkali(ne earth) metal salt present in the polymer. However, from the documents nothing can be learnt in that respect and since there is no mention of removal of stabilisers from the copolymers, a reduction of the alkali(ne earth) metal salt content thereof has not been effected. For completeness' sake it is noted that in GB-A-2249549 there is a single mention of a destabilizing effect of sodium and potassium containing

carbon monoxide and one or more ethylenically unsaturated compounds by reacting the monomers under polymerization conditions in the presence of a suitable catalyst system, one or more components present in the reaction mixture being contaminated with alkali(ne earth) metal salt(s), which process involves a treatment by which at least part of the alkali(ne earth) metal salt is removed such that the total amount of alkali(ne earth) metals present in the copolymerization product is less than 1 part per million by weight.

The invention also relates to a copolymer composition comprising a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds, a contaminant comprising an alkali(ne earth) metal salt and a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate.

Finally, the invention also relates to a method for melt processing a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds, wherein a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds which contains a contaminant comprising an alkali(ne earth) metal salt is mixed with a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate, and wherein the resulting

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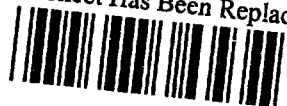


treatment according to this invention effects, in addition to a reduction of the alkali(ne earth) metal content, also a reduction of the content of the accompanying anion of the copolymerization product.

Depending on the origin of the alkali(ne earth) metal salt impurities, the treatment resulting in a decrease in alkali(ne earth) metal content of the copolymers produced, may be carried out after, during or prior to the copolymerization reaction. For example, in the event that the impurities are introduced into the reactor, as contaminants in more than one of the reactor components, the treatment will preferably be carried out during the polymerization reaction.

In the event that the source of alkali(ne earth) metal salt impurities can be attributed to a specific component in the reaction mixture, it is advantageous to subject only that component to the said treatment, prior to its use in the polymerization reaction. For example, if the copolymerization is carried out in the presence of a diluent which is contaminated with alkali(ne earth) metal salts, it is preferred to reduce the alkali(ne earth) metal salt content of the diluent before introducing the diluent into the reactor. Thus, when said treatment is carried out during or prior to the copolymerization reaction and comprises treating one or more alkali(ne earth) metal(s) containing components of the reaction mixture before being introduced into the copolymerization reactor, the alkali(ne earth) metal content of the reaction mixture is reduced.

It has been observed that the alkali(ne earth) metal

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metal content may be up to 100 ppmw. The melt stability of these copolymers is usually unsatisfactory. The treatment of the invention results in a substantial improvement in melt stability of the copolymers and is performed such that the alkali(ne earth) metal content of the copolymers is reduced to less than 1 ppmw and preferably to less than 0.1 ppmw. When said treatment is carried out during or prior to the copolymerization the alkali(ne earth) metal salt(s) is/are preferably removed to such an extent that the alkali(ne earth) metal content of the reaction mixture is below 0.5 ppmw and more preferably below 0.05 ppmw.

For the removal of alkali(ne earth) metal salt(s) various treating methods may be elected. A convenient method may consist in contacting the reaction mixture, or one or more components thereof, such as a contaminated starting material or a contaminated diluent, with a solid material capable of binding or otherwise inactivating the contaminating alkali(ne earth) metal salts, followed by at least partly removal of the alkali(ne earth) metal-enriched solid material.

For example, if a liquid diluent or solvent is used which is contaminated with alkali metal salts, it is recommended to pass the impure liquid through a bed, substantially consisting of solid adsorbent, followed by passing the purified liquid to the reactor. Alternatively, finely divided solid adsorbent particles may be admixed with the contaminated liquid, followed by filtering off the alkali metal-enriched adsorbent particles and introducing the filtrate into the reactor.

enriched adsorbent, when formed during or after the polymerization process, is separated from the copolymers, e.g. by selectively dissolving the latter and removing the alkali(ne earth) metal-enriched adsorbent from the solution. However, only a few solvents are capable of selectively dissolving the copolymers. Therefore it is preferred that a treatment comprising the use of a solid adsorbent is carried out at a stage before the copolymers are formed.

Preferred adsorbents are solid materials, capable of adsorbing, generally as a heterogeneous adsorbent, a major part of the alkali(ne earth) metal ions, such as sodium, lithium and potassium ions, and a major part of the accompanying anions, such as chloride, bromide and acetate ions. Suitable are e.g. ion-exchange resins, zeolites and basic solid materials.

A good adsorbent for the treatment of the invention are apatites, having the general formula $M_{10}(PO_4)_6X_nY_{2-n}$, wherein M is barium, strontium or, preferably, calcium, n is 0, 1 or 2, X is OH and Y is fluorine. Calcium hydroxyapatite is a naturally occurring calcium phosphate, being the major constituent of bone and tooth mineral. It is a crystalline, material, also referred to as tribasic calcium phosphate. However, when the treatment of this invention involves treating a lower aliphatic alcohol, for example methanol, or a mixture containing a substantial quantity of a lower aliphatic alcohol it is less preferred to use an apatite as the adsorbent because, as is known in the art, apatites may

the exchange of anions accompanying the alkali(ne earth) metal a strong basic ion exchange resin can be used, such as a resin containing quaternary ammonium hydroxide groups, for example of the benzyltrimethylammonium type, on a matrix. Very suitably the cation and anion exchange resins are used in a mixed bed or a resin is used which combines the anion and cation exchanging groups on a single matrix. Cross-linked polystyrene is a suitable matrix for ion exchange resins, other matrices being suitable as well. Very suitable systems of one or more ion exchange resins are those which can be used in water demineralisation processes. Very good results have been obtained with a mixed bed ion exchange resin.

Although the amount of solid adsorbent is not critical, usually a limited amount is used, in order to avoid the handling and removal of large amounts of material. Preferably the amount of solid adsorbent is less than 5% by weight of the treated contaminated component(s) of the reaction mixture. Most preferably the amount of solid adsorbent is selected in the range of 0.000001 to 0.5% by weight of the component(s) to be treated.

It may be convenient to use the electrical conductivity as a characterization of liquid components, which are usually essentially organic and non-ionic by nature, after they have been treated with an adsorbent. Suitably the electrical conductivity is lower than 200 μ S/m, preferably less than 100 μ S/m and in particular less than 60 μ S/m. Throughout this application the electrical conductivities are specified as conductivities measured

with a washing liquid which is able to remove alkali(ne earth) metal salts from the copolymer. The invention also relates to a washing per se comprising washing a preformed reactor powder of the copolymer which contains a contaminant comprising an alkali(ne earth) metal salt with a washing liquid which is able to remove at least part of the alkali(ne earth) metal salt(s) from the copolymer, preferably such that after the washing the total amount of alkali(ne earth) metals present in the copolymer is less than 1 part per million by weight.

Suitable washing liquids may be diluents in which the copolymer is insoluble or virtually insoluble and which are substantially free of alkali(ne earth) metal salts, for example by being prior treated with one or more ion exchange resins as described hereinbefore. The washing liquid is suitably essentially organic, polar and non-ionic by nature, for example an aliphatic alcohol or ketone having up to four carbon atoms, and has typically an electrical conductivity of less than 200 $\mu\text{S}/\text{m}$. It may be advantageous to have water present in such a washing liquid, for example 1 - 20 %vol relative to the resultant liquid mixture, with an equal content of alkali(ne earth) metal(s), relative to the total weight of the liquid. The washing liquid may also essentially consisting of water having an electrical conductivity of less than 1000 $\mu\text{S}/\text{m}$, in particular less than 600 $\mu\text{S}/\text{m}$. Very good results can be obtained by washing a copolymer powder, contaminated with alkali(ne earth) metal salt, with methanol or with methanol/water (95/5 v/v) which has prior been made essentially free of alkali(ne earth) metal salt by a

the contaminating alkali(ne earth) metal ion(s) have been added, such as crown ethers.

The catalyst system used in the process of the invention is preferably a catalyst containing one or more metals of Group VIII of the Periodic Table. The amount of such a catalyst is not critical and may vary within wide ranges, e.g. between 10^{-7} and 10^{-2} gram atom of Group VIII metal per mol of ethylenically unsaturated compound to be copolymerized. Preferably the amount is between 10^{-6} and 10^{-4} on the same basis. With a view at their thermal stability copolymers are typically prepared which contain less than 20 ppmw Group VIII metal, preferably less than 10 ppmw and in particular less than 5 ppmw.

The metals of Group VIII include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. Among these, cobalt, nickel, ruthenium, rhodium and palladium are preferred. In particular a catalyst system based on palladium, is preferred.

Very suitable catalyst systems are catalytically active compositions based on a palladium compound, an anion of an acid with a pKa of less than 6, preferably less than 4, and a bidentate ligand.

Preferred bidentate ligands may be indicated by the general formula $R^1R^2M^1-R-M^2R^3R^4$ wherein each of M^1 and M^2 independently represents a phosphorus, arsenic, antimony or nitrogen atom, each of R^1 , R^2 , R^3 and R^4 independently represents a substituted or non-substituted hydrocarbyl group and R represents a divalent organic bridging group containing at least two carbon atoms in the bridge.

or an aromatic group containing one or more substituents, in particular polar substituents such as halogen atoms, halogenated alkyl groups, alkoxy groups such as methoxy, ethoxy or isopropoxy groups, hydroxyl, (di)alkylamino or ester groups.

Preferably one or two substituents are located at the ortho position(s) in the aromatic ring with respect to the phosphorus atom to which that aromatic group is linked.

The copolymerization process of the invention may proceed in the gasphase, but is typically carried out by contacting the monomers in the presence of a suitable diluent with the catalyst system, usually a solution of a compound of a Group VIII metal in a suitable solvent, such as a lower ketone or a lower aliphatic alcohol, for example acetone or methanol. Suitable diluents are typically those in which the formed copolymers are insoluble or virtually insoluble. The diluent is preferably a protic compound, such as an alcohol, for example methanol, isopropanol and butanol-1. As explained above, the diluent may have been subjected to a treatment for reducing the alkali(ne earth) metal content thereof, before being introduced into the reactor.

Ethylenically unsaturated compounds suitable to be copolymerized with carbon monoxide in the process of the invention include compounds consisting exclusively of carbon and hydrogen and compounds which in addition contain one or more heteroatoms, typical examples being unsaturated esters such as methyl acrylate. Preferably, however, unsaturated hydrocarbons are used, in particular

preferred starting materials. The molar ratio between the monomers, viz. carbon monoxide and the ethylenically unsaturated compound(s), is suitably selected in the range of 5:1 to 1:5, preferably in the range of 1.5:1 to 1:1.5.

The copolymerization reaction is suitably carried out at a temperature in the range of 10-200 °C and a pressure in the range of 1 to 200 bar. Preferred temperatures are in the range of 20-180 °C, in particular in the range of 30-150 °C. Preferred pressures are selected in the range of 5 to 100 bar.

In other embodiments of this invention the stability of a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds which is contaminated with an alkali(ne earth) metal salt is improved by using as a stabiliser a substance which is able to bind at least a part of the alkali(ne earth) metal salt. As discussed hereinbefore, the use of a stabilizing quantity of a hydroxyapatite or a zeolite-type trivalent metal silicate in these polymers, conceivably effecting the binding of alkali(ne earth) metal salts in the copolymers, is known in the art and is excluded from the protection of these embodiments of the invention.

The alkali(ne earth) metal salt binding substances used in the compositions of the invention and in the method of melt processing according to the invention may be organic or inorganic. Examples of suitable organic substances may be ion exchange resins mentioned hereinbefore. Inorganic substances which possess ion

when using one or more of barium phosphate, lanthanum phosphate, magnesium orthophosphate, calcium silicium phosphate, magnesium silicium phosphate, aluminium phosphate and fluorapatite (i.e. a mineral of the formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$). Preferred stabilisers are selected from the group consisting of lanthanum phosphate, magnesium silicium phosphate and calcium silicium phosphate.

The quantity of the alkali(ne earth) metal salt binding substances to be used is not critical as long as melt stabilization of the copolymer is effected. Usually a quantity in the range of from 0.01 %w to 5.0 %w, relative to the quantity of the copolymer, will be effective, in particular from 0.02 %w to 1.0 %w and more in particular from 0.05 %w to 0.5 w%, on the same basis.

These substances are frequently solids thus forming a solid phase in the compositions of the invention. They are preferably used as a finely divided material, typically having a volume-average particle size in the range of 0.1 - 50 μm , in particular in the range of 0.5 - 10 μm .

The melt stability of the copolymers may be further improved by adding one or more (further) stabilizers, conveniently by dry blending of the copolymers and the stabilizing compounds, at any downstream stage of the process. Materials known to be suitable in this respect, include inorganic or organometallic compounds, such as zinc aluminates, alumina hydrogels and cupric chromite. As mentioned hereinbefore, calcium hydroxyapatite and calcium containing zeolites have also been recommended as a suitable stabilizer. Also other additives may be

the properties of the resultant blend.

The melt processing according to this invention may be conventional and may include extrusion and injection moulding into sheets, plates and shaped articles.

The invention is illustrated by the following non-limiting experiments and examples.

Experiment 1

The influence of trace quantities of various salts on the melt stability of a linear alternating copolymer of carbon monoxide, ethene and propene was measured as follows.

Samples of the linear alternating copolymer of carbon monoxide, ethene and propene (melting point 222 °C) were loaded with any one of the salts, as indicated in Table I, by impregnating the samples with a solution of the salt in de-ionized (double-distilled) water and drying. For comparison one copolymer sample was treated in the same way with de-ionized water, but without a salt dissolved therein. The resultant copolymer powders were compression moulded to form 1 mm thick sheets by pressing at 250 °C for 0.5 minutes at 4 kg/cm² and 1.5 minutes at 40 kg/cm². Circular discs cut from the sheets were subjected to dynamic rheology testing, i.e. measurement of dynamic shear moduli, at a temperature of 275 °C, using an angular frequency of 1 rad/s and the sample being held between aluminium discs at a distance of 0.9 mm. The aluminium discs were disposable discs, pretreated with an Alodine S solution. The cross-over time (COT), which is defined as the time elapsed since sample loading until the loss factor (i.e. the ratio of

Table I

Salt (metal content of polmer, ppmw)	COT minutes
-	32
Sodium chloride (5.0)	10
Sodium bromide (5.0)	11
Sodium iodide (5.0)	13
Sodium acetate (5.0)	7
Sodium nitrate (5.0)	12
Sodium sulphate (5.0)	23
Sodium perchlorate (5.0)	5
Potassium bromide (8.6)	8
Magnesium sulphate (5.3)	15
Calcium chloride (8.2)	1
Barium bromide (30.2)	2

These experiments show that trace amounts of alkali(ne earth) metal salts contaminating the linear alternating copolymers have a detrimental influence on the copolymers' melt stability.

Experiment 2

The thermal stability of a model compound, representing a carbon monoxide/ethene copolymer, and the influence of (the removal of) trace quantities of alkali(ne earth) metal impurities thereon were measured as follows. The model compound, tetradecan-3,6,9,12-tetraone, was prepared by using methods described by H.

Calcium hydroxyapatite (0.04 g, containing less than 0.1 %w sodium) was suspended in this solution. The resulting suspension was stirred for 1 hour and filtered. The tetradecan-3,6,9,12-tetraone was recovered by evaporating the filtrate to dryness. Sodium analysis of the recovered model compound gave a sodium content of 20 ppmw. The calcium hydroxyapatite remaining on the filter was dried; its sodium content was 0.58 %w.

Samples of the fresh and of the recovered tetradecan-3,6,9,12-tetraone were heated at 240 °C under nitrogen. GLC analysis carried out after 24 hours of heat exposure revealed that the untreated tetradecan-3,6,9,12-tetraone was completely converted (degraded) and that 94 % of the recovered tetradecan-3,6,9,12-tetraone was converted into a range of decomposition products.

The above experiment was repeated using 1 g of a different sample of the tetradecan-3,6,9,12-tetraone and using 0.04 g lanthanum phosphate instead of calcium hydroxyapatite.

Elemental analyses of the fresh and the recovered tetradecan-3,6,9,12-tetraone were as follows: 9 ppmw and 2 ppmw sodium, 3.5 ppmw and 0.6 ppmw calcium, 0.2 ppmw and 0.2 ppmw magnesium, less than 0.5 ppmw and 35 ppmw lanthanum, respectively. The elemental analyses of the fresh and the recovered lanthanum phosphate were as follows: 55 ppmw and 500 ppmw sodium, 45 ppmw and 180 ppmw calcium, less than 30 ppmw and 70 ppmw magnesium, respectively.

GLC analyses after heating the fresh and the recovered tetradecan-3,6,9,12-tetraone (240 °C, 20 hours)

contaminants and that the treatment of the model compound with calcium hydroxyapatite or lanthanum phosphate leads to an improvement in thermal stability. There is also a correlation between the rate of decomposition upon heating at 240 °C and the alkali(ne earth) metal content of the tested samples. It is evident that the melt stability of linear alternating copolymers of carbon monoxide and ethylenically unsaturated compounds can be improved by removing therefrom alkali(ne earth) metal salt contaminants in an analogous way.

Example 1 (for comparison)

A carbon monoxide/ethene copolymer was prepared as follows. A 4000 ml autoclave equipped with a stirrer was charged with 1500 ml methanol/water (95/5 v/v) containing alkali metal salt contaminants and having an electrical conductivity of 360 $\mu\text{S}/\text{m}$. The reactor was closed and the air therein was removed by pressurising with carbon monoxide to 15 bar and releasing the pressure. This procedure of pressurising and pressure release was repeated three times. The temperature in the autoclave was raised to 88 °C and a mixture of carbon monoxide and ethene in a 2:1 ratio was introduced until the pressure was 26 bar. A catalyst solution containing 0.0065 mmol palladium acetate, 0.0069 mmol 1,3-bis[bis(2-methoxyphenyl)phosphinolpropane, 0.0040 mmol trifluoroacetic acid and 4.3 ml acetone was added. The acetone used for preparing the catalyst solution contained alkali metal salt contaminants and had an electrical conductivity of 75 $\mu\text{S}/\text{m}$.

After a period of 17 hours the polymerisation was

in the polymerization, and dried.

A sample of the obtained white polymer powder was compression moulded using substantially the procedure as described in Experiment 1. The sheet obtained was whitish with a grizzly shade.

Example 2

A carbon monoxide/ethene polymer was prepared substantially as described in Example 1, but with the differences that prior to their use in the preparation the methanol/water and the acetone were both percolated over a mixed bed anion/cation exchange resin purchased under the trade name MILLIPORE ION-EX CARTRIDGE. The electrical conductivities of the percolated methanol/water and acetone were 57 $\mu\text{S/m}$ and 38 $\mu\text{S/m}$, respectively.

The obtained polymer powder was white. The sheet obtained by compression moulding this powder was whitish, not having a grizzly shade.

The improved colour of the compression moulded sheet, compared with the colour of the sheet obtained in Example 1 is indicative for an improved thermal stability of the copolymer.

Example 3

A carbon monoxide/ethene polymer was prepared substantially as described in Example 1. A sample of the copolymer powder obtained was washed four times with methanol which methanol was prior percolated over a mixed bed anion/cation exchange resin purchased under the trade name MILLIPORE ION-EX CARTRIDGE. The electrical conductivity of the percolated methanol was 23 $\mu\text{S/m}$.

The electrical conductivities of the washing liquids obtained in each washing were 650 $\mu\text{S/m}$, 200 $\mu\text{S/m}$, 60 $\mu\text{S/m}$ and 52 $\mu\text{S/m}$, respectively, indicating that alkali metal salt impurities were removed from the copolymer in each of the washings.

For comparison a sheet was compression moulded from a sample of the un-washed copolymer and a circular disc cut from the sheet was subjected to the dynamic rheology testing. The cross-over time was 14 minutes.

The improved thermal stability of the washed sample is evident from a comparison of the cross-over times.

Examples 4 - 13

Samples of a linear alternating copolymer of carbon monoxide, ethene and propene (melting point 222 °C), which was contaminated with alkali metal salt, were powder blended with 0.25 %w or 0.20 %w (calculated on the weight of the composition) of any one of the phosphates indicated in Table II. The resultant powder mixtures were compression moulded and tested in dynamic rheology testing substantially as described in Experiment 1. For comparison a sample of the copolymer was tested un-blended. The cross-over times (COT) found are indicated in Table II.

4	- *)	22
5	Calcium hydroxyapatite (0.25) *)	39
6	Lanthanum phosphate (0.25)	39
7	Barium phosphate (0.25)	33
8	Calcium fluorapatite (0.25)	28
9	Magnesium orthophosphate (0.20)	37
10	Calcium phosphate (0.20)	31
11	Calcium silicium phosphate (0.20)	39
12	Magnesium silicium phosphate (0.20)	30
13	Aluminium phosphate (0.20)	29

*) for comparison, not according to invention

1. A process for the preparation of linear alternating copolymers of carbon monoxide and one or more ethylenically unsaturated compounds by reacting the monomers under polymerization conditions in the presence of a suitable catalyst system, one or more components present in the reaction mixture being contaminated with alkali(ne earth) metal salt(s), which process involves a treatment by which at least part of the alkali(ne earth) metal salt is removed such that the total amount of alkali(ne earth) metals present in the copolymerization product is less than 1 part per million by weight.
2. A process as claimed in claim 1, characterized in that the total amount of alkali(ne earth) metals is less than 0.1 part per million by weight.
3. A process as claimed in claim 1 or 2, characterized in that said treatment is carried out during or prior to the copolymerization reaction and comprises treating one or more alkali(ne earth) metal(s) containing components of the reaction mixture before being introduced into the copolymerization reactor.
4. A process as claimed in claim 3, characterized in that the said treatment consists in contacting one or more of the components of the reaction mixture with a solid adsorbent, capable of adsorbing ions of alkali(ne earth) metal salts, followed by at least partly removal of alkali(ne earth) metal-enriched adsorbent.
5. A process as claimed in claim 4, characterized in that the solid adsorbent comprises one or more ion exchange resins containing anion exchanging and cation exchanging groups on a matrix, optionally combined on a

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7. A process as claimed in claim 1 or 2, characterized in that the copolymer powder as prepared in the reactor is washed with a washing liquid which is able to remove alkali(ne earth) metal salts from the copolymer, such as a diluent in which the copolymer is insoluble or virtually insoluble and which has an electrical conductivity of less than 200 $\mu\text{S/m}$.

8. A process as claimed in any of claims 1 - 7, characterized in that the catalyst system contains at least one metal of Group VIII of the Periodic Table and is used in an amount such that per mol of ethylenically unsaturated compound to be copolymerized it contains 10^{-6} - 10^{-4} gram atom of Group VIII metal.

9. A process as claimed in claim 8, characterized in that a catalyst system is used which is based on palladium as Group VIII metal, an anion of an acid with a pK_a of less than 4 and a bidentate ligand of the general formula $\text{R}^1\text{R}^2\text{M}^1\text{-R-M}^2\text{R}^3\text{R}^4$ wherein each of M^1 and M^2 independently represents a phosphorus, arsenic, antimony or nitrogen atom, each of R^1 , R^2 , R^3 and R^4 independently represents a substituted or non-substituted hydrocarbyl group and R represents a divalent organic bridging group containing at least two carbon atoms in the bridge.

10. A process as claimed in claim 9, characterized in that a catalyst system is used comprising a bidentate ligand of the general formula $\text{R}^1\text{R}^2\text{P-R-PR}^3\text{R}^4$ wherein at least one of R^1 , R^2 , R^3 and R^4 represents an aromatic group substituted by a polar group, in particular an alkoxy group, at one or both ortho positions with respect to the phosphorus atom to which the aromatic group is



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used, in that the molar ratio between carbon monoxide on the one hand and the ethylenically unsaturated compound(s) on the other, is in the range from 5:1 to 1:5, in particular in the range from 1.5:1 to 1:1.5, and in that the reaction is carried out in the presence of a protic diluent, for example methanol, at a temperature in the range of 30 - 150 °C and at a pressure in the range of 5 to 100 bar.

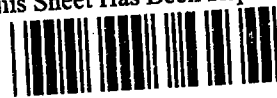
12. A method for improving the melt stability of a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds comprising washing a preformed reactor powder of the copolymer which contains a contaminant comprising an alkali(ne earth) metal salt with a washing liquid which is able to remove at least part of the alkali(ne earth) metal salt(s) from the copolymer.

13. A copolymer composition comprising a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds, a contaminant comprising an alkali(ne earth) metal salt and a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate.

14. A copolymer composition as claimed in claim 13, characterized in that the substance which is able to bind at least part of the alkali(ne earth) metal salt is selected from the group consisting of barium phosphate, lanthanum phosphate, magnesium orthophosphate, calcium silicium phosphate, magnesium silicium phosphate,



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selected from the group consisting of lanthanum phosphate, magnesium silicium phosphate and calcium silicium phosphate.

16. A copolymer composition as claimed in any of claims 13 - 15, characterized in that the substance which is able to bind at least part of the alkali(ne earth) metal salt is used in a quantity of in the range of from 0.02 %w to 1.0 w%, relative to the quantity of the copolymer.

17. A copolymer composition as claimed in claim 16, characterized in that the substance which is able to bind at least part of the alkali(ne earth) metal salt is used in a quantity of in the range of from 0.05 %w to 0.5 w%, relative to the quantity of the copolymer.

18. A method for melt processing a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds, wherein a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds which contains a contaminant comprising an alkali(ne earth) metal salt is mixed with a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate, and wherein the resulting mixture is melt processed, such as by extrusion or injection moulding.

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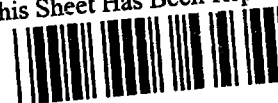


PREPARATION OF COPOLYMERS OF CARBON MONOXIDE
WITH ETHYLENICALLY UNSATURATED COMPOUNDS, COMPOSITION
AND METHOD FOR MELT PROCESSING

A process for the preparation of linear alternating copolymers of carbon monoxide and an ethylenically unsaturated compound by polymerizing the monomers in the presence of a suitable catalyst system, one or more components present in the reaction mixture being contaminated with alkali(ne earth) metal salt(s), which process involves a treatment by which at least part of the alkali(ne earth) metal salt is removed such that the total amount of alkali(ne earth) metals present in the copolymerization product is less than 1 part per million by weight; a copolymer composition comprising said copolymer, an alkali(ne earth) metal salt contaminant and a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate; and a method for melt processing said copolymer, wherein the copolymer which contains an alkali(ne earth) metal salt contaminant is mixed with a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite or a zeolite-type trivalent metal silicate, and wherein the resulting mixture is melt processed.

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Accordingly, the invention relates to a process for the preparation of linear alternating copolymers of carbon monoxide
5 and one or more ethylenically unsaturated compounds by reacting the monomers under polymerization conditions in the presence of a suitable catalyst system, one or more components present in the reaction mixture being contaminated with alkali(ne earth) metal salt(s), which process involves a treatment by which at
10 least part of the alkali(ne earth) metal salt is removed such that the total amount of alkali(ne earth) metals present in the copolymerization product is decreased, on the understanding that the treatment does not consist of adding to the copolymerization product of a hydroxy apatite, a zinc aluminate, an alumina
15 hydrogel or a decomposition product thereof, or a zeolite-type trivalent metal silicate.

The invention also provides a method for improving the melt stability of a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds comprising
20 washing a preformed reactor powder of the copolymer which contains a contaminant comprising an alkali(ne earth) metal salt with a washing liquid which is able to remove at least part of the alkali(ne earth) metal salt(s) from the copolymer.

The invention also relates to a copolymer composition
25 comprising a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds, a contaminant comprising an alkali(ne earth) metal salt and a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than
30 a hydroxyapatite, a zinc aluminate, an alumina hydrogel or a decomposition product thereof, or a zeolite-type trivalent metal silicate.

Finally, the invention also relates to a method for melt processing a linear alternating copolymer of carbon monoxide and
35 one or more ethylenically unsaturated compounds, wherein a linear alternating copolymer of carbon monoxide and one or more

5 being other than a hydroxyapatite, a zinc aluminate, an aluminium hydrogel or a decomposition product thereof, or a zeolite-type trivalent metal silicate, and wherein the resulting mixture is melt processed, such as by extrusion or injection moulding.

chloride, sodium acetate or sodium silicate, the treatment according to this invention effects, in addition to a reduction of the alkali(ne earth) metal content, also a reduction of the content of the accompanying anion of the copolymerization product.

Depending on the origin of the alkali(ne earth) metal salt impurities, the treatment resulting in a decrease in alkali(ne earth) metal content of the copolymers produced, may be carried out after, during or prior to the copolymerization reaction. For example, in the event that the impurities are introduced into the reactor, as contaminants in more than one of the reactor components, the treatment will preferably be carried out during the polymerization reaction.

In the event that the source of alkali(ne earth) metal salt impurities can be attributed to a specific component in the reaction mixture, it is advantageous to subject only that component to the said treatment, prior to its use in the polymerization reaction. For example, if the copolymerization is carried out in the presence of a diluent which is contaminated with alkali(ne earth) metal salts, it is preferred to reduce the alkali(ne earth) metal salt content of the diluent before introducing the diluent into the reactor. Thus, when said treatment is carried out during or prior to the copolymerization reaction and comprises treating one or more alkali(ne earth) metal(s) containing components of the reaction mixture before being introduced into the copolymerization reactor, the alkali(ne earth) metal content of the reaction mixture is reduced.

It has been observed that the alkali(ne earth) metal

1. A process for the preparation of linear alternating copolymers of carbon monoxide and one or more ethylenically unsaturated compounds by reacting the monomers under polymerization conditions in the presence of a suitable catalyst system, one or more components present in the reaction mixture being contaminated with alkali(ne earth) metal salt(s), which process involves a treatment by which at least part of the alkali(ne earth) metal salt is removed such that the total amount of alkali(ne earth) metals present in the copolymerization product is decreased, on the understanding that the treatment does not consist of adding to the copolymerization product a hydroxy apatite, a zinc aluminate, an alumina hydrogel or a decomposition product thereof, or a zeolite-type trivalent metal silicate.
2. A process as claimed in claim 1, characterized in that in the copolymerization product the total amount of alkali(ne earth) metals is less than 1 part per million by weight.
3. A process as claimed in claim 2, characterized in that the total amount of alkali(ne earth) metals is less than 0.1 part per million by weight.
4. A process as claimed in any of claims 1-3, characterized in that said treatment is carried out during or prior to the copolymerization reaction and comprises treating one or more alkali(ne earth) metal(s) containing components of the reaction mixture before being introduced into the copolymerization reactor.
5. A process as claimed in claim 4, characterized in that the said treatment consists in contacting one or

of alkali(ne earth) metal-enriched adsorbent.

6. A process as claimed in claim 5, characterized in that the solid adsorbent comprises one or more ion exchange resins containing anion exchanging and cation exchanging groups on a matrix, optionally combined on a single matrix.

7. A process as claimed in claim 5 or 6, characterized in that the amount of solid adsorbent is in the range of 0.000001 to 0.5% by weight of the component(s) treated.

8. A process as claimed in any of claims 1-7, characterized in that the catalyst system contains at least one metal of Group VIII of the Periodic Table and is used in an amount such that per mol of ethylenically unsaturated compound to be copolymerized it contains 10^{-6} - 10^{-4} gram atom of Group VIII metal.

9. A process as claimed in claim 8, characterized in that a catalyst system is used which is based on palladium as Group VIII metal, an anion of an acid with a pKa of less than 4 and a bidentate ligand of the general formula $R^1R^2M^1-R-M^2R^3R^4$ wherein each of M^1 and M^2 independently represents a phosphorus, arsenic, antimony or nitrogen atom, each of R^1 , R^2 , R^3 and R^4 independently represents a substituted or non-substituted hydrocarbyl group and R represents a divalent organic bridging group containing at least two carbon atoms in the bridge.

10. A process as claimed in claim 9, characterized in that a catalyst system is used comprising a bidentate ligand of the general formula $R^1R^2P-R-PR^3R^4$ wherein at least one of R^1 , R^2 , R^3 and R^4 represents an aromatic group substituted by a polar group, in particular an alkoxy group, at one or both ortho positions with respect

characterized in that as ethylenically unsaturated compound ethene or a mixture of ethene and propene is used, in that the molar ratio between carbon monoxide on the one hand and the ethylenically unsaturated compound(s) on the other, is in the range from 5:1 to 1:5, in particular in the range from 1.5:1 to 1:1.5, and in that the reaction is carried out in the presence of a protic diluent, for example methanol, at a temperature in the range of 30-150 °C and at a pressure in the range of 5 to 100 bar.

12. A method for improving the melt stability of a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds comprising washing a preformed reactor powder of the copolymer which contains a contaminant comprising an alkali(ne earth) metal salt with a washing liquid which is able to remove at least part of the alkali(ne earth) metal salt(s) from the copolymer.

13. A copolymer composition comprising a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds, a contaminant comprising an alkali(ne earth) metal salt and a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite, a zinc aluminate, an alumina hydrogel or a decomposition product thereof, or a zeolite-type trivalent metal silicate.

14. A copolymer composition as claimed in claim 13, characterized in that the substance which is able to bind at least part of the alkali(ne earth) metal salt is selected from the group consisting of barium phosphate,

15. A copolymer composition as claimed in claim 14, characterized in that the substance which is able to bind at least part of the alkali(ne earth) metal salt is selected from the group consisting of lanthanum phosphate, magnesium silicium phosphate and calcium silicium phosphate.

16. A copolymer composition as claimed in any of claims 13-15, characterized in that the substance which is able to bind at least part of the alkali(ne earth) metal salt is used in a quantity of in the range of from 0.02 %w to 1.0 w%, relative to the quantity of the copolymer.

17. A copolymer composition as claimed in claim 16, characterized in that the substance which is able to bind at least part of the alkali(ne earth) metal salt is used in a quantity of in the range of from 0.05 %w to 0.5 w%, relative to the quantity of the copolymer.

18. A method for melt processing a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds, wherein a linear alternating copolymer of carbon monoxide and one or more ethylenically unsaturated compounds which contains a contaminant comprising an alkali(ne earth) metal salt is mixed with a stabilizing quantity of a substance which is able to bind at least part of the alkali(ne earth) metal salt, the substance being other than a hydroxyapatite, a zinc aluminate, an aluminium hydrogel or a decomposition product thereof, or a zeolite-type trivalent metal silicate, and wherein the resulting mixture is melt processed, such as by extrusion or injection moulding.