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COMPLETE SPECIFICATION

Process for the Preparation of Olefinic Copolymers

We, MONTECATINI SOCIETÀ GENERALE PER L'INDUSTRIE MINERARIA E CHIMICA, a Body Corporate organised and existing under the laws of Italy, of 1—2, Largo Guido Donegani, Milan, Italy, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In the Specification of our co-pending application No. 14144/63 1022755 there are described and claimed vulcanisable, high molecular weight, substantially linear, amorphous copolymers of dialkenyl- or multi-alkenyl-cycloalkanes having from 3 to 5 or 6 carbon atoms in the cycloalkane ring and at least one terminal double bond with ethylene and/or one or more aliphatic alpha-olefins having the general formula $R-CH=CH_2$, in which R is an alkyl group containing from 1 to 6 carbon atoms, which copolymers substantially consist of macromolecules containing monomeric units deriving from each of the monomers used and unsaturations.

As is described in said specification such copolymers are obtainable with the aid of halogen containing catalysts, acting with an anionic co-ordinated mechanism, and prepared from transition metal compounds, in particular vanadium compounds and organometallic compounds of metals of groups I, II, and III of the Periodic Table according to Mendeleef or complex organometallic compounds of metals of groups I and III, wherein the valencies of the metal were saturated with organic groups, halogen atoms or oxygen atoms bound to an organic group.

We have now found that the above mentioned copolymers may also be obtained when for the preparation of the catalyst, hydrides of metals of Groups I, II and III of complex

hydrides of metals of Groups I and III are used.

The invention provides a process for the preparation of high molecular weight linear unsaturated amorphous copolymers of one or more monomers having the general formula $R-CH=CH_2$, wherein R is a hydrogen atom or an alkyl group containing from 1 to 6 carbon atoms with di- or multi-alkenylcycloalkanes, which comprises polymerising a mixture of said monomers in the presence of a catalyst comprising the reaction product of a compound of a transition metal of group IV or V of the Periodic Table according to Mendeleef and a hydride of a metal of Groups I, II or III or a complex hydride of a metal of Group I or III.

Examples of suitable compounds are: lithium hydride, alkylaluminium hydrides (e.g. diethyl-aluminiummonohydride, diisobutyl-aluminiummonohydride, monoethylaluminiumdihydride), aluminiumhalohydrides (e.g. aluminiumchlorohydride), lithium-aluminium alkylhydrides (e.g. diisobutylolithiumaluminiumhydride), lithium-aluminium hydride, zinc hydride and calcium hydride.

Vanadium compounds are preferably used with these compounds in the preparation of the catalyst.

In order to obtain copolymers having a highly homogeneous composition it is advisable to use hydrocarbon-soluble vanadium compounds.

Therefore there are preferably used, vanadium halides and oxy-halides (such as VCl_3 , $VOCl_3$, VBr_3) and those compounds wherein at least one of the valencies of the metal is saturated by a heteroatom (particularly oxygen or nitrogen) bound to an organic group as for instance vanadium triacetylacetonate and tribenzoylacetonate, vanadyl diacetylacetonate,

haloacetylacetonates, trialcoholates and haloalcoholates, tetrahydrofuranates, etherates aminates, pyridinates and quinolinates of vanadium tri- and tetrachloride and of vanadyl trichloride.

Hydrocarbon insoluble vanadium organic salts such as vanadium tribenzoate and vanadium tristearate may also be used.

The catalysts are therefore those obtained by reacting a vanadium compound and a hydride where at least one of the valencies of vanadium and/or at least one of the valencies of the metal of the hydride compound are saturated by a halogen atom.

The copolymerisation can be carried out in the presence of an inert aliphatic, cycloaliphatic or aromatic hydrocarbon solvent. Halogen-containing hydrocarbon compounds can, if desired, also be used as solvents.

The copolymerisation may be carried out at temperatures of from -80 to 125°C . Particularly high copolymerisation rates may be obtained if the polymerisation is carried out in the absence of an inert solvent, using the monomers themselves in the liquid state, for instance in the presence of a solution of ethylene in the mixture of alpha-olefins and di- or multialkenyl cycloalkane to be copolymerised, kept in the liquid state.

In order to obtain copolymers having a highly homogeneous composition, it is advisable to keep the ratio between the concentrations of the monomers to be polymerised present in the liquid reacting phase constant or at least as constant as possible during the copolymerisation.

To this end it may be convenient to carry out the copolymerisation in a continuous way, by continuously feeding and discharging a mixture of monomers having a constant composition and by working with high spatial rates.

The olefins which may be employed have the general formula $\text{R}-\text{CH}=\text{CH}_2$ wherein R is a hydrogen atom or an alkyl group containing from 1 to 6 carbon atoms.

Suitable di- or multialkenyl-cycloalkanes are *trans* 1,2 - divinylcyclobutane, *cis* - 1,2 - divinylcyclobutane; 1,2 - divinylcyclopentane; *trans* - divinylcyclopropane; 1,2 - divinylcyclohexane; trivinylcyclohexanes, diallylcyclohexanes, 1 - vinyl - 2 - *isopropenyl* - cyclobutane; 1,2 divinyl - 1,2 - dimethyl cyclobutane and 1 - vinyl - 1 - methyl - 2 - *isopropenyl* cyclobutane, for example.

By varying the composition of the mixture of the monomers, it is possible to vary the composition of the copolymers within wide limits.

If the amorphous copolymers of ethylene with a di- or multialkenyl cycloalkane are desired, it is necessary to regulate the mixture of the monomers in such a way as to obtain copolymers having a relatively high cycloalkane content, preferably higher than 25 mols %.

If, on the other hand, amorphous copolymers with ethylene and propylene are desired, it is advisable to maintain in the reacting liquid phase a molar ratio between ethylene and propylene lower than or at most equal to 1:4 which corresponds to a molar ratio between ethylene and propylene in the gaseous phase, under normal conditions, lower than or at most equal to 1:1. Molar ratios comprised between 1:200 and 1:4 in the liquid phase are generally satisfactory.

If butene-1 is used instead of propylene, the molar ratio between ethylene and butene must be lower than or at most equal to 1:20; the composition of the corresponding gaseous phase under normal conditions is lower than or at most equal to 1:1.5. Molar ratios in the liquid phase comprised between 1:1000 and 1:20 are generally satisfactory.

By operating under these conditions amorphous terpolymers are obtained which contain less than 75 mol % of ethylene. With higher ethylene contents the terpolymer shows a poly-ethylenic type crystallinity.

The ethylene lower limit is not critical although it is generally preferred that the terpolymers contain at least 5 mols % of ethylene. The alpha olefin content in the amorphous terpolymer may range from a minimum of 5 mols % up to a maximum value of 95 mols %.

It is in general convenient, more particularly for economical reasons, to introduce into the terpolymer a total cycloalkane amount lower than 20 mols %. Cycloalkane amounts between 0.1 and 20% are usually preferred.

The copolymers prepared by the process of the invention have the properties of non-vulcanized elastomers since they show low initial elastic moduli and have very high elongations at break.

The presence of unsaturations in the macromolecules which form these copolymers make possible their vulcanization, by using the methods generally known for unsaturated rubbers, particularly for those having low unsaturations. The vulcanized products show high reversible elastic elongations, and particularly when reinforcing fillers such as carbon black are used in the mix they also have high tensile strength.

The elastomers obtained by vulcanization of the copolymers may be advantageously used, due to their high mechanical characteristics in all the application fields of natural and synthetic rubbers.

The following Examples are given to illustrate the invention. In view of the use of phenyl-beta-naphthylamine it should be mentioned that there is thought to be a connection between some naphthylamines and the cause of some cases of cancer.

EXAMPLE 1.

The reaction apparatus comprises a glass

- cylinder having a diameter of 5.5 cm and a capacity of 750 cc, provided with an agitator and gas inlet and outlet tubes, immersed in a thermostatic bath at -20°C .
- 5 The gas inlet tube reaches the bottom of the cylinder and ends in a porous diaphragm (diameter 3.5 cm).
- Into the reactor, kept under nitrogen, 200 cc of anhydrous *n*-heptane and 7 cc of *trans* 1,2-divinylcyclobutane are introduced.
- 10 Through the gas inlet tube a gaseous mixture of propylene and ethylene in a molar ratio of 2:1 is introduced and circulated at a flow-rate of 200 N litres/hour.
- 15 In a 100 cc flask kept under nitrogen, the catalyst is prepared at -20°C by reacting 1 millimol of vanadium tetrachloride and 5 millimols of aluminium diethylmonohydride in 30 cc of anhydrous *n*-heptane.
- 20 The catalyst thus prepared is siphoned into the reactor under nitrogen pressure. The propylene/ethylene mixture is continuously fed and discharged at a rate of 400 N litres/h.
- 25 After 15 minutes, the reaction is stopped by addition of 20 cc of methanol containing 0.1 g of phenyl-beta-naphthylamine.
- The product is purified in a separating funnel, under nitrogen, by repeated treatments with diluted hydrochloric acid and then with water and is finally coagulated with acetone.
- 30 After vacuum drying, 5 grams of solid product are obtained which appear amorphous under X-rays, looks like a non-vulcanized elastomer and is completely soluble in boiling *n*-heptane.
- The infrared spectographic examination shows the presence of vinyl groups (bands at 10 and 11 microns). The ethylene/propylene molar ratio in the copolymer obtained is about 1:1.
- 40 100 parts by weight of the copolymer are mixed in a laboratory roll mixer with 1 part of phenyl beta-naphthylamine, 2 parts of sulphur, 5 parts of zinc oxide, 1 part of tetramethylthiuramdisulphide and 0.5 parts of mercaptobenzothiazole. The mixture thus obtained is vulcanized in a press for 30 minutes at 150°C .
- 50 A vulcanized lamina having the following characteristics is obtained:
- | | |
|---------------------|-----------------------|
| tensile strength | 25 kg/cm ² |
| elongation at break | 500% |
| modulus at 300% | 13 kg/cm ² |
- 55 **EXAMPLE 2.**
- The reaction apparatus is a glass cylinder having a capacity of 700 cc and a diameter of 5.5 cm provided with an agitator and gas inlet and outlet tubes.
- 60 The gas inlet tube reaches the bottom of the cylinder and ends in a porous diaphragm (diameter 3.5 cm).
- 200 cc of anhydrous *n*-heptane and 15 cc of 1-2-4 tri-vinyl-cyclohexane are introduced into the apparatus which is kept at -20°C .
- 65 Through the gas inlet tube a propylene-ethylene-mixture in a molar ratio of 2:1 is introduced and circulated at a flow-rate of 200 Nl/h.
- In a 100 cc flask kept under nitrogen at -20°C , the catalyst is pre-formed by reacting 0.5 millimols of vanadium tetrachloride with 2.5 millimols of aluminium diethylmonohydride in 30 cc of *n*-heptane.
- 70 The catalyst thus pre-formed is siphoned into the reactor by means of nitrogen pressure.
- The ethylene-propylene gaseous mixture is continuously fed and discharged at a flow-rate of 400 Nl/h.
- 80 After 8 minutes, the reaction is stopped by addition of 20 cc of methanol containing 0.1 g of phenyl - beta - naphthylamine.
- The product is purified in a separating funnel under nitrogen by repeated treatments with aqueous hydrochloric acid and then with water and is then coagulated in acetone.
- 85 After vacuum drying, 20 g of a solid product which is amorphous by X-ray examination, looks like a non-vulcanized elastomer and is completely soluble in boiling *n*-heptane are obtained.
- The intrinsic viscosity, determined in toluene at 30°C is 1.6.
- 90 The infrared spectographic examination shows the presence of vinyl groups (bands at 10 and 11 microns). The ethylene-propylene molar ratio is about 1.
- 100 parts by weight of ethylene-propylene-trivinyl-cyclohexane terpolymer are mixed in a laboratory roll mixer with 1 part of phenyl-beta-naphthylamine, 2 parts of sulphur, 5 parts of zinc oxide, 1 part of tetramethylthiuram disulphide, and 0.5 parts of mercaptobenzothiazole. The mix is vulcanized in a press at 150°C for 60 minutes.
- 105 A vulcanized sheet having the following characteristics is thus obtained:
- | | |
|---------------------|-----------------------|
| tensile strength | 27 kg/cm ² |
| elongation at break | 400% |
| modulus at 300% | 12 kg/cm ² |
- 110 **EXAMPLE 3**
- 200 cc of anhydrous *n*-heptane and 7 cc of *trans* 1-2-divinyl cyclobutane are introduced into the reaction apparatus described in Example 1, kept at -20°C .
- 115 Through the gas inlet tube, a propylene-ethylene mixture in a molar ratio of 3:1 is introduced and circulated at a flow-rate of 200 Nl/h.
- 120 The catalyst is pre-formed at -20°C under nitrogen by reacting 1 millimol of vanadium oxytrichloride with 5 millimols of aluminium diisobutyl monohydride in 30 cc of anhydrous *n*-heptane.
- 125 The catalyst thus pre-formed is siphoned into the reactor by means of a nitrogen pressure.

The propylene-ethylene mixture is continuously fed and discharged at a flowrate of 400 NI/h.

5 After 10 minutes the reaction is stopped by adding 10 cc of methanol containing 0.1 g of phenyl-beta-naphthylamine.

10 The product is purified and isolated as described in Example 1. After vacuum drying, 14 g of a solid product which is amorphous by X-ray examination, looks like a non-vulcanized elastomer and is completely soluble in boiling *n*-heptane are obtained.

15 The infrared spectrographic examination shows the presence of vinyl groups (bands at 10 and 11 microns).

The ethylene-propylene molar ratio is about 1:1.

20 The product is vulcanized as described in Example 1. A vulcanized sheet having the following characteristics is thus obtained:

tensile strength	35 kg/cm ²
elongation at break	540%
modulus at 300%	13 kg/cm ²

EXAMPLE 4

25 200 cc of anhydrous *n*-heptane and 15 cc of 1-2-4 tri-vinylcyclohexane are introduced into the reaction apparatus described in Example 1, kept at -20°C.

30 Through the gas inlet tube, a propylene-ethylene mixture in a molar ratio of 2:1 is introduced and circulated at a flow-rate of 200 NI/h.

35 The catalyst is preformed at -20°C under nitrogen by reacting 0.5 millimols of vanadium tetrachloride with 2.5 millimols of aluminium diisobutylmonohydride in 30 cc of anhydrous *n*-heptane.

40 The catalyst, thus preformed, is siphoned into the reactor by means of a nitrogen pressure.

The propylene-ethylene mixture is continuously fed and discharged at a flow-rate of 400 NI/h.

45 After 7 minutes the reaction is stopped by adding 20 cc of methanol containing 0.1 g of phenyl-beta-naphthylamine.

50 The product is purified and isolated as described in Example 1. After vacuum drying, 12 g of a solid product which is amorphous by X-ray examination, looks like a non-vulcanized elastomer and is completely soluble in boiling *n*-heptane are obtained.

55 The infrared spectrographic examination shows the presence of vinyl groups (bands at 10 and 11 microns). The ethylene-propylene molar ratio, is about 1:1.

The product is vulcanized as described in Example 1. A vulcanized sheet having the following characteristics thus obtained:

60 tensile strength	32 kg/cm ²
elongation at break	540%
modulus at 300%	13 kg/cm ²

EXAMPLE 5

200 cc of anhydrous *n*-heptane and 7 cc of *trans* 1-2-divinylcyclobutane are introduced 65 into the reaction apparatus described in Example 1, kept at -20°C.

70 Through the gas inlet tube a propylene-ethylene mixture in a molar ratio of 2:1 is introduced and circulated at a flow-rate of 200 NI/h.

75 The catalyst is preformed at -20°C under nitrogen by reacting 2 millimols of vanadium tetrachloride and 5 millimols of lithium aluminium diisobutylhydride in 30 cc of anhydrous *n*-heptane.

80 The catalyst thus pre-formed is siphoned into the reactor by means of a nitrogen pressure. The propylene-ethylene mixture is continuously fed and discharged at a flow-rate of 400 NI/h.

After 50 minutes, the reaction is stopped by adding 10 cc of methanol containing 0.1 g of phenyl-beta-naphthylamine.

85 The product is purified and isolated as described in Example 1.

90 After vacuum drying, 4 g of a solid product which is amorphous by X-ray examination, looks like a non-vulcanized elastomer and is completely soluble in boiling *n*-heptane are obtained.

The infrared spectrographic examination shows the presence of vinyl groups (bands at 10 and 11 microns).

95 The ethylene/propylene molar ratio is about 1:1.

100 The product is vulcanized as described in Example 1, and gives a vulcanized product having the same characteristics as the product obtained in Example 1.

WHAT WE CLAIM IS:—

1. A process for the preparation of high molecular weight linear unsaturated amorphous copolymers of one or more monomers having the general formula R-CH=CH₂, 105 wherein R is a hydrogen atom or an alkyl group containing from 1 to 6 carbon atoms with di- or multi-alkenyl-cycloalkanes having from 3 to 5 or 6 carbon atoms in the cycloalkane ring and at least one terminal double bond, which copolymers substantially consist of macromolecules containing monomeric units deriving from each of the monomers used and unsaturations, which comprises polymerising a mixture of said monomers in the presence of a halogen containing catalyst comprising the reaction product of a compound of a transition metal of Group IV or V of the Periodic Table according to Mendeleef and a hydride of a metal of Groups I, II or III or a complex hydride of a metal of Group I or III. 110 115 120

2. A process according to Claim 1 in which lithium hydride, an aluminium alkylhydride, an aluminium halohydride a lithium-aluminium alkylhydride, lithium aluminium hydride, zinc 125

- hydride, or calcium hydride is used in the preparation of the catalyst.
3. A process according to claim 1 or claim 2 in which the transition metal is vanadium.
- 5 4. A process according to claim 3 in which a hydrocarbon soluble vanadium compound is used.
5. A process according to claim 4 in which the vanadium compound is a halide, oxyhalide 10 or a compound in which at least one of the valencies of the metal is saturated by an heteroatom, in particular oxygen or nitrogen, bound to an organic group.
6. A process according to claim 3 in which 15 a hydrocarboninsoluble vanadium organic salt is employed.
7. A process according to claim 6 in which the salt is vanadium triacetate, tribenzoate or tristearate.
8. A process according to any of the preceding claims in which the polymerisation is carried out at a temperature of from -80 to 125°C . 20
9. A process for the preparation of linear unsaturated copolymers substantially as herein described in any of the Examples. 25
10. Linear, amorphous, vulcanizable, high molecular weight copolymers obtained by the process of any of the preceding claims.
11. Elastomers obtained by vulcanizing the 30 copolymers claimed in claim 10.

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