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(54) **HYDROGENATION DE POLYMERES INSATURES CONTENANT DES GROUPES NITRILES**

(54) **HYDROGENATION OF UNSATURATED POLYMERS CONTAINING NITRILE GROUPS**

(57) Hydrogenation products of olefinically unsaturated polymers having nitrite groups prepared in the presence of ruthenium catalysts in a solvent comprising a low-molecular ketone and a secondary or tertiary C_3-C_6-alcohol by hydrogenation, can be processed to vulcanizates with improved compression set values.

Hydrogenation of unsaturated polymers containing nitrile groups

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A b s t r a c t

Hydrogenation products of olefinically unsaturated polymers having nitrile groups prepared in the presence of ruthenium catalysts in a solvent comprising a low-molecular ketone and a secondary or tertiary C_3-C_6-alcohol by hydrogenation, can be processed to vulcanizates with improved compression set values.

Patent claim

Process for the selective hydrogenation of olefinically unsaturated polymers containing nitrile groups with hydrogen in the presence of a hydrogenation catalyst in an organic solvent,

characterized in that

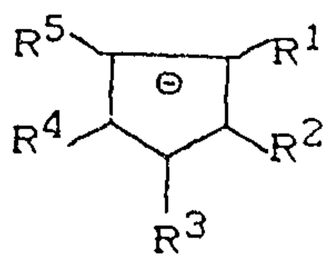
(i) the hydrogenation catalyst used is a ruthenium compound of the formula

$$RuX_{2y}\,[(L^1)_n\,(L^2)_{5-z}] \qquad (I)$$

wherein

X denotes hydrogen, halogen or $SnCl_3$,

L^1 denotes hydrogen, halogen, $(R^6\text{-}COO)_n$ or cyclopentadienyl of the formula



in which R^1 to R^5 independently of one another represent hydrogen, methyl, ethyl or phenyl, it also being possible for adjacent substituents together to form a hydrocarbon radical such that L^1 is an indenyl or afluorenyl system,

L^2 denotes a phosphane, bisphosphane or arsane and

y denotes zero, 0.5 or 1,

n denotes 1 or 2,

z denotes an integer from 1 to 4 and

R^6 denotes alkyl, cycloalkyl, aryl or aralkyl having 1 to 20 C atoms,

and

(ii) the solvent used is a mixture of

a) a C_3-C_6 ketone and

b) a monohydric secondary or tertiary C_3-C_6-alcohol, the weight content of b) in the solvent (ii) being 2 to 60.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the selective hydrogenation of olefinically unsaturated polymers containing nitrile groups with hydrogen in the presence of a hydrogenation catalyst in an organic solvent,

characterized in that

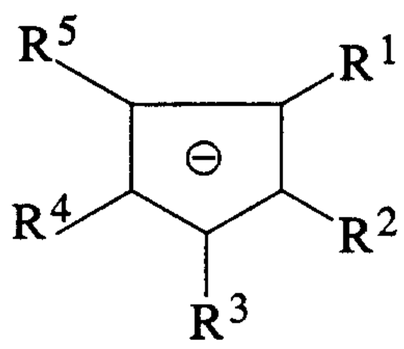
(i) the hydrogenation catalyst used is a ruthenium compound of the formula

$$RuX_{2y}\,[(L^1)_n\,(L^2)_{5-z}] \qquad (I)$$

wherein

X denotes hydrogen, halogen or $SnCl_3$,

L^1 denotes hydrogen, halogen, $(R^6\text{-}COO)_n$ or cyclopentadienyl of the formula



in which R^1 to R^5 independently of one another represent hydrogen, methyl, ethyl or phenyl, it also being possible for adjacent substituents together to form a hydrocarbon radical such that L^1 is an indenyl or a fluorenyl system,

L^2 denotes a phosphane, bisphosphane or arsane and

y denotes zero, 0.5 or 1,

n denotes 1 or 2,

z denotes an integer from 1 to 4 and

R^6 denotes alkyl, cycloalkyl, aryl or aralkyl having 1 to 20 C atoms,

and

(ii) the solvent used is a mixture of

a) a C_3-C_6 ketone and

b) a monohydric secondary or tertiary C_3-C_6-alcohol, the weight content of b) in the solvent (ii) being 2 to 60%.

2. A process according to claim 1 wherein said weight content of b) in solvent (ii) is 5 to 50%.

3. A process according to claim 1 wherein said weight content of b) in solvent (ii) is 7 to 40%.

4. A process according to any one of claims 1 to 3 wherein the ligand L^1 is selected from cyclopentadienyl, pentamethylcyclopentadienyl, ethyltetramethylcyclopentadienyl, pentaphenylcyclopentadienyl, dimethyltriphenylcyclopentadienyl, indenyl and fluorenyl.

5. A process according to any one of claims 1 to 3 wherein R^6 is selected from methyl, ethyl, propyl, iso-propyl, tert.-butyl, cyclohexyl, phenyl, benzyl and trifluoromethyl.

6. A process according to any one of claims 1 to 5

wherein L^2 is selected from triphenylphosphane, diethylphenyl-phosphane, tritolylphosphane, trinaphthylphosphane, diphenylmethylphosphane, diphenylbutylphosphane, tris-(p-carbomethoxyphenyl)-phosphane, tris-(p-cyanophenyl)-phosphane, tributylphosphane, tris-(trimethoxyphenyl)-phosphane, bis-(trimethylphenyl)-phenylphosphane, bis-(trimethoxyphenyl)-phenylphosphane, trimethylphenyl-diphenylphosphane, trimethoxyphenyldiphenylphosphane, tris-(dimethylphenyl)-phenylphosphane, tris-(dimethoxyphenyl)-phosphane, bis-(dimethylphenyl)-phenylphosphane, bis-(dimethoxyphenyl)-phenylphosphane, dimethylphenyldiphenylphosphane, dimethoxyphenyldiphenylphosphane, triphenylarsane, ditolylphenylarsane, tris-(4-ethoxyphenyl)-arsane, diphenylcyclohexylarsane, dibutylphenylarsane and diethylphenylarsane.

7. A process according to any one of claims 1 to 5 wherein L^2 is triphenylphosphane.

8. A process according to claim 1, 2 or 3 wherein the compound of formula I is

$RuCl_2(PPh_3)_3$

$RuHCl(PPh_3)_3$

$RuH_2(PPh_3)_4$

$RuH_4(PPH_3)_3$

$RuH(CH_3COO)(PPh_3)_3$

$RuH(C_2H_5COO)(PPh_3)_3$

$RuH[(CH_3)_3C.COO](PPh_3)_3$

$Ru(CH_3COO)_2(PPh_3)_2$

$RuCl(Cp)(PPh_3)_2$

$RuH(Cp)(PPh_3)_2$

$Ru(SnCl_3)(Cp)(PPh_3)_2$

$RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2$

$RuH(\eta^5\text{-}C_9H_7)(PPh_3)_2$

$Ru(SnCl_3)(\eta^5\text{-}C_9H_7)(PPh_3)_2$

$RuCl(\eta^5\text{-}C_{13}H_9)(PPh_3)_2$

$RuH(\eta^5\text{-}C_{13}H_9)(PPh_3)_2$

$Ru(SnCl_3)(\eta^5\text{-}C_{13}H_9)(PPh_3)_2$ or

$RuCl(\eta^5\text{-}C_9H_7)$(dppe) in which "Ph" denotes phenyl, "Cp" denotes cyclopentadienyl and "dppe" denotes 1,2-bis-diphenylphosphanoethane.

9. A process according to any one of claims 1 to 8 wherein the solvent component a) is selected from acetone, butanone, pentanone, cyclopentanone and cyclohexanone and mixtures thereof.

10. A process according to any one of claims 1 to 8 wherein the solvent component a) is butanone or acetone.

11. A process according to any one of claims 1 to 10 wherein the solvent component b) is selected from 2-propanol, 2-butanol, 2-methyl-2-propanol, 2- and 3-pentanol, 3-methyl-2-

butanol, 2-methyl-2-butanol, 2-, 3- and 4-hexanol and 4-methyl-2-pentanol.

12. A process according to any one of claims 1 to 10 wherein the solvent component b) is selected from 2-methyl-2-propanol, 2-butanol, and 2-propanol.

13. A process according to any one of claims 1 to 12 wherein the concentration of the catalyst is 2 to 500 ppm based on the polymer and calculated as Ruthenium.

14. A process according to any one of claims 1 to 12 wherein the concentration of the catalyst is 5 to 300 ppm based on the polymer and calculated as Ruthenium.

15. A process according to any one of claims 1 to 14 wherein the hydrogenation is effected at 20 to 250°C and under a hydrogen pressure of 1 to 350 bar.

16. A process according to any one of claims 1 to 14 wherein the hydrogenation is effected at 120 to 160°C and under a hydrogen pressure of 10 to 200 bar.

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