

The present invention relates to new polyaryl-alkane oligomer compositions and to a process for their manufacture.

5 These products can be used as a microencapsulation solvent for carbonless transfer paper.

 In Patent EP 136,230, the person skilled in the art has already proposed mixtures of oligomers based on benzyltoluene, dibenzyltoluene and ditolylphenylmethane,
10 which exhibit the advantage, when compared with these same oligomers taken separately, of crystallising at very low temperature and of having a viscosity which is always compatible with their application as a dielectric for capacitors. These characteristics makes [sic] them most
15 particularly suitable for use as a microencapsulation solvent for carbonless transfer paper; nevertheless they have a characteristic which disqualifies them in the case of a use of this kind, namely a highly unpleasant odour which is disclosed just like the colour at the time of
20 hitting the keys of a typewriter, for example. The compositions according to the invention not only have a viscosity which is compatible with the application, but are also characterised by an "absence of odour" which is absolutely essential in the intended application.

25 Patent GB 1,346,364 summarises the properties which must be reconciled in microencapsulation solvents:

- dissolving the dye
- not evaporating when the microcapsules are processed
- 30 - being inert towards the encapsulation material
- not reacting with the solvent [sic] developer
- having a viscosity which is low and relatively insensitive to temperature, and
- not having an unpleasant odour.

35 Since the disadvantages of mono- and dibenzyl alkylbenzenes have also long been known, many substitute mixtures have been proposed, starting with polyarylalkane oligomers. However, it is always difficult to reconcile the quality of the properties of the products obtained

with the economic aspect of the means for producing this substitute product.

Thus, Japanese Patent Application JP-Kokai 73-86, 612 describes the use of di(propylbenzyl)propyl-
5 benzene, the synthesis of which calls for a large number of reaction and separation stages due to the nonselectivity of a synthesis of this type.

Lastly, in Japanese Patent Application JP-Kokai 78-42,909 reference is made to the use, as a microencapsulation solvent, of the following isomers:
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- ditolylphenylmethane
- tolyldiphenylmethane
- tritolylphenylmethane

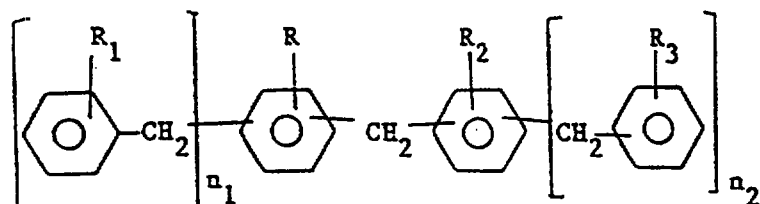
The synthesis of each of these isomers calls for
15 specific reactions, for example tolyldiphenylmethane from benzylidene chloride, toluene and benzene, followed by a separation of the isomers; moreover, a mixture of these products must then be produced, and this is hardly advantageous from the standpoint of economy.

As a general rule, the prior art shows products
20 for the microencapsulation solvent application, of the monobenzylalkylbenzene or dibenzylalkylbenzene, or alternatively di(alkylphenyl)phenylmethane type, but which can be manufactured only using relatively nonselective syntheses.
25

The present invention proposes products which are adapted for the microencapsulation solvent application and which have the advantage of being capable of being manufactured in a simple manner.

30 The present invention relates to polyarylalkane oligomer compositions consisting of the mixture of two oligomers A and B, which are characterised in that:

- the oligomer A is a mixture of isomers of formula:



in which:

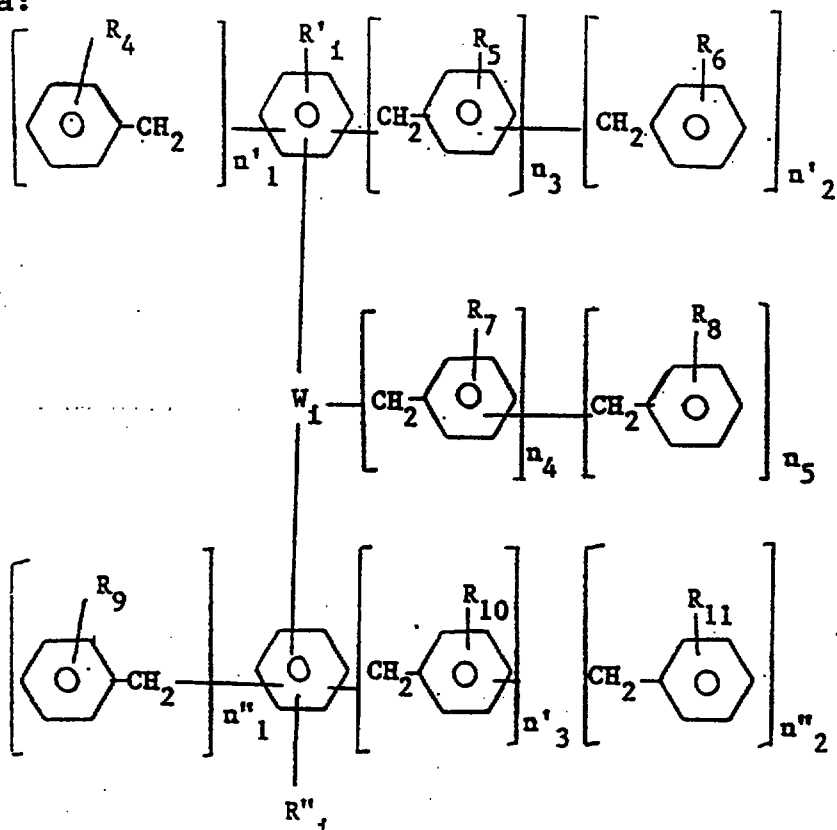
R is a linear or branched hydrocarbon chain containing n carbon atoms, and n is between 2 and 16

5 R_1, R_2 and R_3 are identical or different and
denote H or CH_3

$$n_1 \text{ and } n_2 = 0, 1 \text{ and } 2 \text{ with } n_1 + n_2 \leq 3$$

it being possible for each of the isomers A to have different substituents R, R₁, R₂ and R₃:

10 - the oligomer B is a mixture of isomers of formula:



in which

R'_i and R''_i are identical or different and have the same meaning as R_i .

$R_4, R_5, R_6, R_7, R_8, R_9, R_{10},$ and R_{11} are identical or different and denote H or CH_3 ,

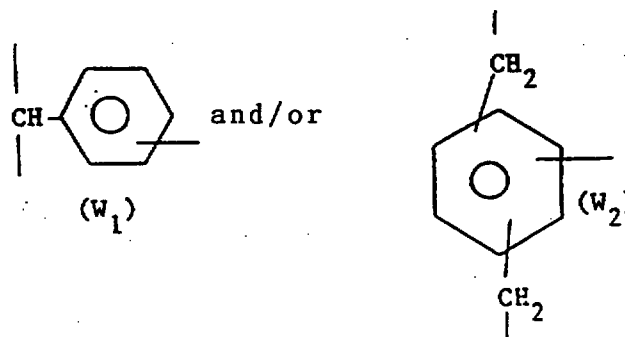
n'_1, n''_1 and $n_4 = 0, 1$ or 2 ,

n'_2, n''_2, n_3, n'_3 and $n_5 = 0$ or 1 ,

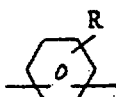
5 $n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 \leq 2$

i has the value of 1 or 2,

W_i is a trivalent connecting group such as:



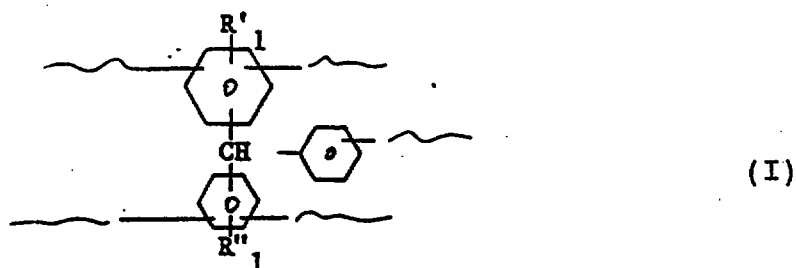
and in which the connections towards the groups

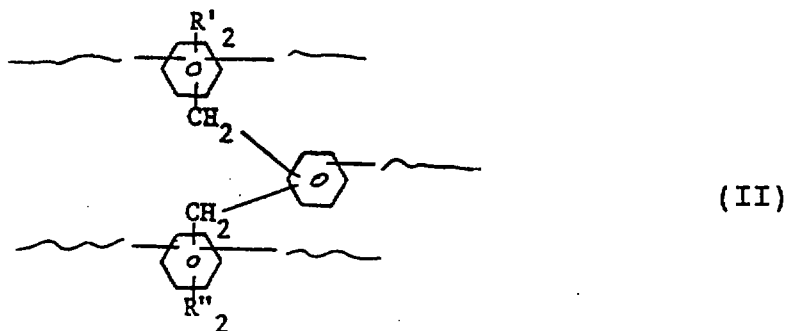


10 are provided by carbon atoms not forming part of the phenyl group of W_i ,

it being possible for each of the isomers B to have different substituents R'_1, R''_1 , and R_4 to R_{11} .

15 That is to say that B may be a mixture of the products of formula (I) and (II), each of the products (I) and (II) itself being a mixture of isomers.





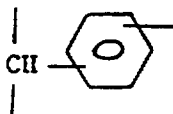
Among the compositions of the invention use is advantageously made of those or [sic] R , R'_1 and R''_1 are alkyls with n between 3 and 8, and preferably isopropyls.

Compositions in which R_1 and R_{11} are hydrogen atoms are also advantageously employed.

Compositions in which R_1 to R_{11} are hydrogen atoms and R , R'_1 and R''_1 are alkyls with n between 3 and 8, and preferably isopropyl groups, are also advantageously employed.

The particularly preferred compositions are such that:

- R_1 to R_{11} are hydrogens
- R , R'_1 and R''_1 are isopropyls
- i has the value of 1, that is to say that the connecting group W_1 is:



The compositions according to the invention exhibit all the properties which must be reconciled in microencapsulation solvents and the Applicant Company has found to its surprise that these products are not odorants.

The compositions according to the invention may be obtained by employing a process which calls only for chlorine, toluene, xylene and the product of formula (III)  in which Y is a linear or branched hydrocarbon chain containing from 2 to 16 carbon atoms, as starting materials. The product of formula (III) may also be a mixture of products which have different

chains Y.

A process for obtaining the oligomer compositions according to the invention is characterised in that, in a first stage, chlorine is reacted with toluene or xylene or a mixture of toluene and xylene by a radical reaction in the presence of a radical generator, and then any unreacted toluene or xylene is removed and, in a second stage, the reaction product from this first stage is subjected to the action of an inorganic halide or of an inorganic acid in the presence of a product of formula (III) or of a mixture of products (III) which have different chains Y.

The starting hydrocarbon in the first stage is either toluene or xylene, or a mixture of toluene and xylene.

The radical chlorination of the hydrocarbon is usually carried out at a temperature of between 50 and 110°C and, better, between 70 and 100°C. It is preferably conducted so that only 10 to 30 %, expressed as a molar percentage, of the hydrocarbon employed is converted into the corresponding chlorine derivative. The unconverted hydrocarbon is then removed, for example by distillation. The free radical generator employed may be either a photochemical initiation or a chemical initiator; among the chemical initiators there may be mentioned azo compounds such as azodiisobutyronitrile or else azo-divaleronitrile, and peroxides such as, for example, lauroyl peroxide. The quantity of chemical initiator which is employed is generally between 0.05 and 3 % by weight relative to the hydrocarbon employed, and preferably between 0.1 and 1.5 %.

The reaction mixture obtained during the first stage is then subjected, in the presence of the product of formula (III) to the action of an inorganic halide, or else of an inorganic acid. In practice, this reaction takes place at a temperature of between 30 and 140°C, and preferably between 50 and 120°C.

A single product of formula (III) or a mixture of products (III) which have different chains Y may be employed.

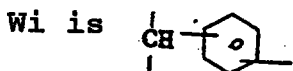
5 The product (III) or mixtures thereof are advantageously added to the mixture obtained at the end of the first stage after the removal of the toluene and/or xylene.

10 Preferably, as many moles of product (III) are added as are removed in the form of toluene and/or xylene.

15 Among the inorganic halides, it is possible to employ ferric chloride, antimony trichloride, titanium tetrachloride or else aluminium chloride in weight concentrations, relative to the reaction mixture, which are generally between 50 ppm and 1 %, and preferably between 100 ppm and 0.5 %. Inorganic acids may also be employed: for example, sulphuric acid at a concentration of between 70 and 95 % by weight. It is also possible to employ zeolites or, alternatively, certain inorganic
20 oxides. An alternative form of the process in this second stage consists in pouring the reaction mixture from the first stage into the product (III) or the product (III) and the mixture of oligomers according to the invention, containing the inorganic halide or acid in the form of a
25 solution or a dispersion; this alternative form is particularly advantageous for operating a continuous process of this kind, since it is obvious that this synthesis can be carried out noncontinuously or continuously.

30 After the excess product (III) has been distilled off, the removal of the inorganic halide or of the inorganic acid may be carried out by any known method such as: washing with water, neutralisation and drying.

35 Toluene is advantageously employed in the first stage, and the groups R_1 to R_{11} (in the oligomers according to the invention) are then hydrogen atoms, and



Advantageously, the product of formula (III) is an alkylbenzene, Y containing from 3 to 8 carbon atoms, and R, R' and R", are then alkyls. Isopropylbenzene (or cumere [sic]) is preferably employed, that is to say that
5 Y is an isopropyl group, and the groups R, R', and R", are then identical and denote an isopropyl.

According to the process described, the mixture of polyaryllalkane oligomers is generally obtained directly in the following proportions by weight:

10 Compound A as a mixture of isomers:

$$n_1 + n_2 = 0 \text{ between } 56 \text{ and } 90 \%$$

$$n_1 + n_2 = 1 \text{ between } 7 \text{ and } 28 \%$$

$$n_1 + n_2 = 2 \text{ between } 1.5 \text{ and } 8 \%$$

$$n_1 + n_2 = 3 \text{ between } 0.1 \text{ and } 3 \%$$

15 Compound B as a mixture of isomers:

$$n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 0$$

between 1.1 and 5 %

$$n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 1$$

between 0.25 and 1.5 %

20 $n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 2$
between 0.05 and 0.5 %

Depending on the use to which the mixture of polyaryllalkane oligomers according to the invention is applied, it may be advantageous to perform a flash
25 evaporation of this mixture to remove traces of impurities originating either from the starting materials or from the process, or having an incidental origin; in all cases the contents by weight do not exceed 1 to 2 %. Among the pieces of equipment which can be employed,
30 preference will be given to a thin-film evaporator; it must be reported, however, that, on an industrial scale, the technical performance of such equipment in respect of behaviour under vacuum does not always allow all of the mixture of polyaryllalkane oligomers to be recovered:
35 these evaporated products nevertheless form an integral part of the invention, as is the case particularly with the isomers of the compound A for $n_1 + n_2 = 3$ and of the compound B for $n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4$

+ n_5 = 2.

The following examples illustrate the invention without limiting it.

EXAMPLE 1

5 368 g of toluene (4 moles) are placed in a reactor equipped with stirring a condenser [sic], a chlorine feed tube and a Philips TLADK 30-watt lamp; 71 g of gaseous chlorine (1 mole) are then introduced while the temperature is maintained at 80°C for 1 hour.

10 After stopping the photochemical initiation, the reaction mixture is placed in a 1-litre three-necked round bottom flask supporting an adiabatic glass column filled with a packing of glass helices (approximately 10 plates). The mixture is subjected to a fractional distil-
15 lation under a vacuum of 50 mm of mercury so as to separate the unreacted toluene. The distillation is stopped when the toluene content at the foot of the column is below 0.2 % (temperature equal to 100°C).

20 The product recovered as the distillation residue is placed in a dropping funnel and is introduced over one hour into a reactor equipped with stirring, containing 600 g of cumene (5 moles) and 60 mg of FeCl₃ at a temperature of 100°C. The whole is kept at 100°C, with stirring, for another 1 hour after the end of addition.

25 After cooling, the reaction mixture is washed with 10 % hydrochloric acid and then with water until neutral and, lastly, the excess cumene is removed by distillation under a vacuum of 10 mm [sic] of mercury through a column of a few plates, so that the residual
30 content of cumene in the bottom product is below 500 ppm (bottom temperature at the end of distillation = 180°C).

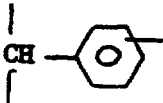
The mixture of polyaryllalkane oligomers obtained has the following composition by weight:

PRODUCT	$n_1 + n_2$				$n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5$			
	0	1	2	3	0	1	2	
A	68.8	20.8	4.2	2.5	-	-	-	
B	-	-	-	-	2.4	1	0.3	

And its formula is such that:

$$R = R'_i = R''_i = CH(CH_3)_2$$

$$R_1 \text{ to } R_{11} = H$$

$i = 1$, that is to say W_1 is 

5 The overall weight yield calculated relative to the cumene which has reacted is 97 %.

When subjected to a flash evaporation at 300°C at 1 mm of Hg, this product gives, in a 95 % yield, a mixture of polyaryllalkaneoligomers with a very faint odour and whose composition differs from that given above
10 in the absence of the products corresponding to:

$$A \text{ and } n_1 + n_2 = 3$$

$$b \text{ and } n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 2$$

15 For a viscosity:

$$\text{at } 20^\circ\text{C} = 9.5 \text{ cP}$$

$$\text{at } 40^\circ\text{C} = 4.40 \text{ cP}$$

EXAMPLE 2

Operating under the same conditions of Example 1,
20 but using 6 moles of toluene (592 g) for the photochlorination per 1 mole of chlorine and 9 moles of cumere [sic] in the coupling reaction, a mixture of polyaryllalkane oligomers of the same formula as in Example 1 and having the following composition by weight is obtained:

PRODUCT	$n_1 + n_2$				$n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5$							
	0	1	2	3	0	1	2	3	4	5	6	7
A	83 %	11 %	2.8 %	0.7 %	-	-	-	-	-	-	-	-
B	-	-	-	-	2 %	0.4 %	0.1 %	-	-	-	-	-

The weight yield calculated relative to cumere [sic] is 98 %.

When subjected to a flash evaporation at 300°C at 1 mm of Hg, this product gives, in a 98% yield, a mixture of polyaryllalkane oligomers with a very faint odour and whose composition differs from that given above in the absence of the products corresponding to:

A and $n_1 + n_2 = 3$

B and $n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 2$

For a viscosity at:

20°C = 6.9 cP

40°C = 3.9 cP

EXAMPLE 3

Operating under the same conditions as Example 1, but replacing the cumene with 5 moles of ethylbenzene (530 g) in the coupling reaction.

The polyaryllalkane oligomer mixture obtained has the following compositions by weight:

PRODUCT	$n_1 + n_2$				$n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5$		
	0	1	2	3	0	1	2
A	67	22.3	4.4	2.6	-	-	-
B	-	-	-	-	2.4	0.9	0.4

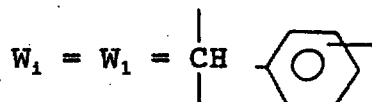
The weight yield calculated relative to ethylbenzene is 98 %.

And a formula in which:

$$R, R'_1, R''_1 = C_2H_5$$

$$R_1, \text{ to } R_{11} = H$$

$$i = 1$$



10 When subjected to a flash evaporation at 300°C at 1 mm of Hg, this product gives, in a 96% yield, a mixture of polyaryllalkane oligomers with a faint odour, whose composition differs from that given above in the absence of the products corresponding to:

15 A and $n_1 + n_2 = 3$

B and $n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 2$

For a viscosity at:

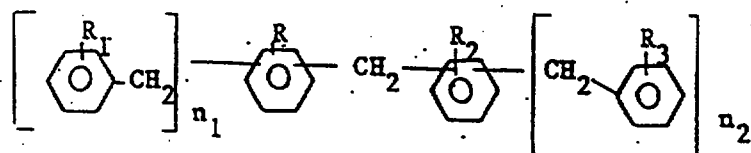
$$20^\circ\text{C} = 6.9 \text{ cP}$$

$$40^\circ\text{C} = 4.2 \text{ cP}$$

CLAIMS

1. Polyaryllalkane oligomer compositions consisting of the mixture of two oligomers A and B, which are characterised in that:

5 - the oligomer A is a mixture of isomers of formula:



in which:

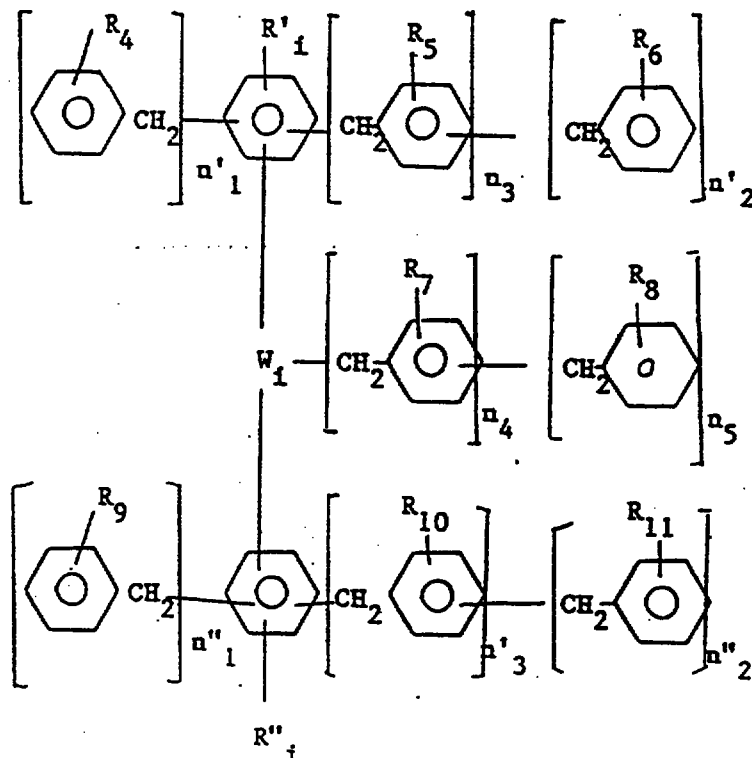
R is a linear or branched hydrocarbon chain containing n carbon atoms, and n is between 2 and 16

10 R₁, R₂ and R₃ are identical or different and denote H or CH₃

n₁ and n₂ = 0, 1 and 2 with n₁ + n₂ ≤ 3

it being possible for each of the isomers A to have different substituents R, R₁, R₂ and R₃:

15 - the oligomer B is a mixture of isomers of formula:



in which:

R'_1 and R''_1 are identical or different and have the same meaning as R ,

5 $R_4, R_5, R_6, R_7, R_8, R_9, R_{10}$ and R_{11} are identical or different and denote H or CH_3 ,

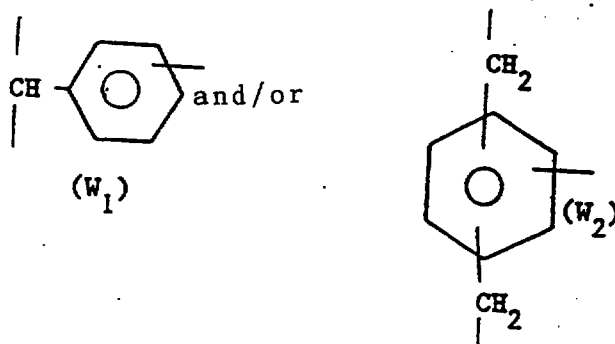
n'_1, n''_1 and $n_4 = 0, 1$ or 2 ,

n'_2, n''_2, n_3, n'_3 and $n_5 = 0$ or 1 ,

$n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 \leq 2$

i has the value of 1 or 2 ,

10 W_i is a trivalent connecting group such as:



and in which the connections towards the groups



are provided by carbon atoms not forming part of the phenyl group of W_i , it being possible for each of the isomers B to have different substituents R'_1, R''_1 , and R_4 to R_{11} .

15

2. Compositions according to Claim 1, characterised in that R, R'_1 and R''_1 are alkyls with n between 3 and 8, and preferably isopropyls.

20

3. Compositions according to Claims 1 or 2, characterised in that R_1 to R_{11} are hydrogen atoms.

4. Compositions according to Claim 1, characterised in that:

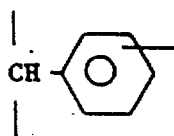
- R_1 to R_{11} are hydrogens

- R, R'_1 and R''_1 are isopropyls and

25

- i has the value of 1 , that is to say that the

connecting group W_i is:



5. Compositions according to Claim 4, characterised in that the mixture of oligomers is in the proportions by weight of:

Compound A as a mixture of isomers:

5 $n_1 + n_2 = 0$ between 56 and 90 %

$n_1 + n_2 = 1$ between 7 and 28 %

$n_1 + n_2 = 2$ between 1.5 and 8 %

$n_1 + n_2 = 3$ between 0.1 and 3 %

Compound B as a mixture of isomers:

10 $n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 0$
between 1.1 and 5 %

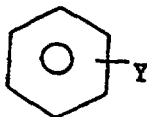
$n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 1$
between 0.25 and 1.5 %

15 $n'_1 + n''_1 + n'_2 + n''_2 + n_3 + n'_3 + n_4 + n_5 = 2$
between 0.05 and 0.5 %

6. Process for the manufacture of polyaryllalkane oligomer compositions according to Claim 1, characterised in that, in a first stage, chlorine is reacted with toluene or xylene or a mixture of toluene and xylene in the presence of a radical generator, and then the unreacted toluene or xylene or the unreacted toluene and xylene are removed and, in a second stage, the reaction product from this first stage is subjected to the action of an inorganic halide or of an inorganic acid in the presence of a benzene-related product of formula:

20

25



(III)

in which Y is a linear or branched hydrocarbon chain containing from 2 to 16 carbon atoms or a mixture of such benzene-related products.

30 7. Process according to Claim 6, characterised in that, in the first stage, only 10 to 30 mol% of the toluene or xylene or of the mixture of toluene and xylene which is employed is converted into a chlorine

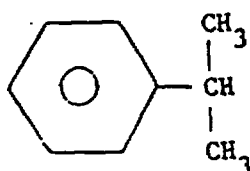


derivative.

8. Process according to Claim 6 or 7, characterised in that, in the first stage, chlorine is reacted with toluene.

5 9. Process according to one of Claims 6 to 8, characterised in that the product of formula (III) is an alkylbenzene, Y containing from 3 to 8 carbon atoms, or a mixture of such alkylbenzenes.

10 10. Process according to one of Claims 6 to 9, characterised in that the product of formula (III) is



(isopropylbenzene or cumene).

11. Process according to one of Claims 6 to 10, characterised in that a flash evaporation is carried out on the product obtained in the second stage.

