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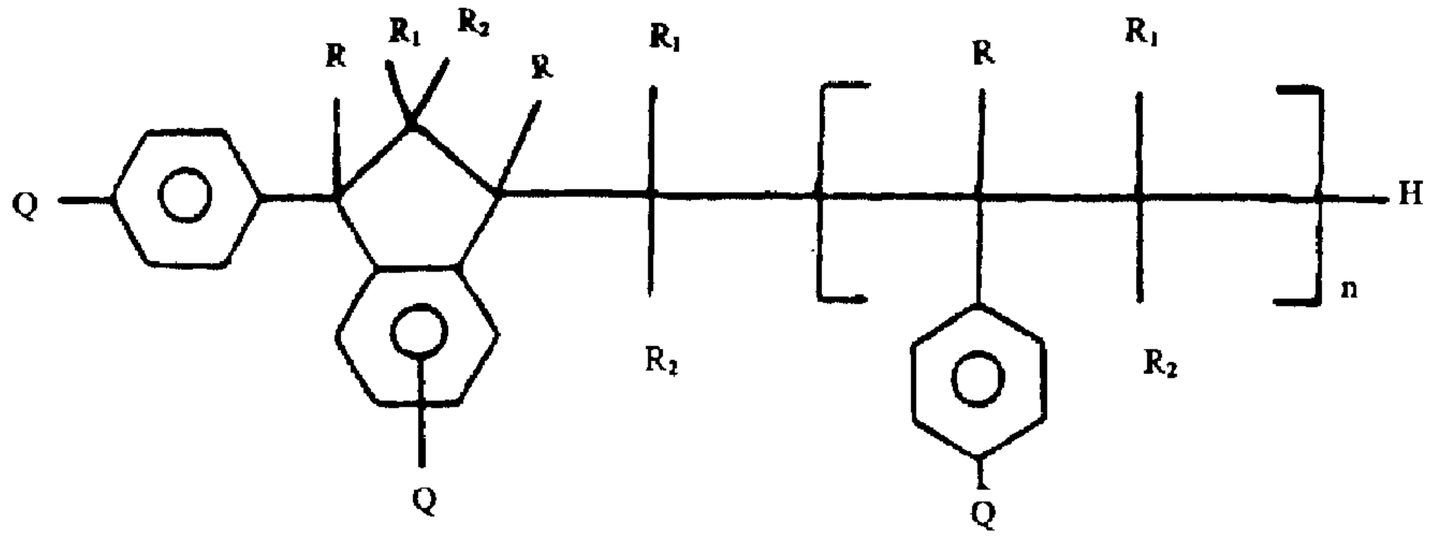
(54) Title: STABLE LIQUID COMPOSITIONS USEFUL AS POLYMERIZATION PHOTO-PROMOTERS, THEIR PREPARATION AND USE



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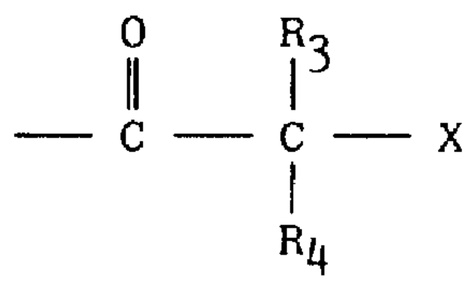

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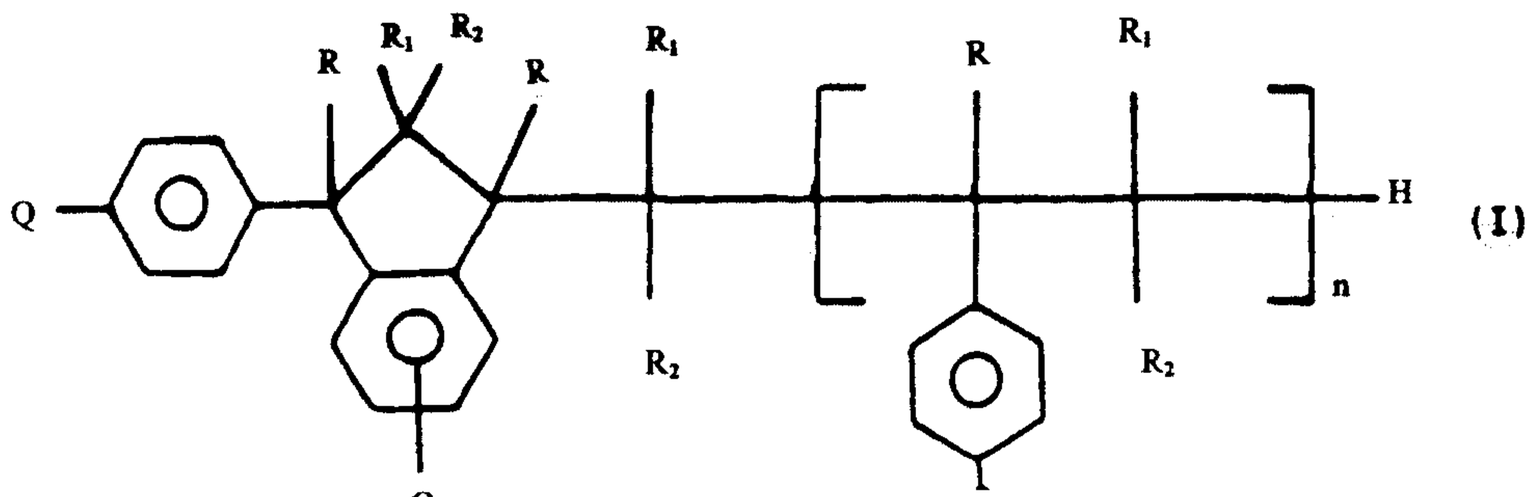
(57) Abrégé/Abstract:
Disclosed is a stable liquid composition containing between 25 and 75 parts by weight of at least one solvent chosen from the group consisting of xylene, methylethyl ketone, butyl acetate, an optionally ethoxylated acrylic ester of a glycol or of a polyol, N-vinyl pyrrolidone, alphahydroxy isobutyrrophenone, a liquid benzophenone and diethoxyacetophenone, and containing between 25 and 75 parts by weight of at least one 1-phenylindan carbonyl derivative, whose structure is represented by the formula: (see formula I) wherein: n is from 0 to 1; R, R_1, R_2 are the same or different, and each independently represents H or C_1-C_3 alkyl; Q represents a group (see formula II) in which R_3 and R_4 are the same or different, and either each is independently a C_1-C_8 alkyl group; or together they can be a C_3-C_7 polyalkylene group; or together they can coincide in an oxygen atom; and X is Cl, OH, or OR in which R has the same meaning as defined above before.

ABSTRACT

Disclosed is a stable liquid composition containing between 25 and 75 parts by weight of at least one solvent chosen from the group consisting of xylene, methylethyl ketone, butyl acetate, an optionally ethoxylated acrylic ester of a glycol or of a polyol, N-vinyl pyrrolidone, alphahydroxy isobutyrrophenone, a liquid benzophenone and diethoxyacetophenone, and containing between 25 and 75 parts by weight of at least one 1-phenylindan carbonyl derivative, whose structure is represented by the formula:



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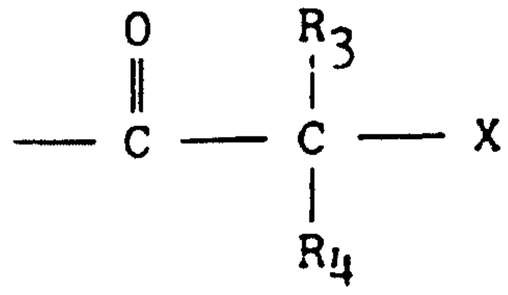
wherein:

n is from 0 to 1;

R, R_1, R_2 are the same or different, and each independently represents H or C_1-C_3 alkyl;

Q represents a group



in which R_3 and R_4 are the same or different, and either each is independently a C_1-C_8 alkyl group; or

together they can be a C_3-C_7 polyalkylene group; or

together they can coincide in an oxygen atom; and

X is Cl, OH, or OR in which R has the same meaning as defined above before.

STABLE LIQUID COMPOSITIONS USEFUL AS POLYMERIZATION PHOTO-PROMOTERS, THEIR PREPARATION AND USE

DESCRIPTION

A. Technical Background

The present invention refers to new stable liquid compositions suitable for use as photo-promoters for photo-polymerizing compounds or mixtures of compounds containing ethylenic double bonds, and their preparation and use.

The photo-chemical polymerization of unsaturated monomers and prepolymers is today a widely known process with a large number of industrial applications.

This type of reaction occurs due to the interaction between light energy in a well defined range of the electromagnetic spectrum, and a suitable substratum capable of absorbing the light and polymerizing. This irradiation causes, through various mechanisms depending on the nature of the substances present, the generation of radical type groups, which, within a very short time, give rise to a polymerisation reaction of the molecules containing ethylenic double bonds. To facilitate the absorbtion of light and the creation of radical groups, photo-sensitizing and photo-promoting substances in particular are generally used.

The photo-sensitizing substances are used to absorb and transfer luminous energy whenever a photo-promoter does not absorb energy in the spectrum regions useful for the photo-chemical reaction being carried out, the photo-promoters are used to generate radicals that

promote polymerization.

The efficiency of these products has been steadily improved as technological processes using photo-polymerization have become more widespread, as in the case of paints and lacquers, printing inks, the manufacture of printing plates and electronic circuits, silk screens for printing on ceramics and textiles, transfers, and for use in dentistry. The efficiency of these products is measured by their reactivity, intended both as quantum yield (the quantity of monomer converted for each quantum of light absorbed), as polymerization rate (the time required for a substrate to reach determined chemico/physical properties), and also the stablilty in the dark of mixtures containing a photo-promoter.

B. Prior Art

1-Phenylindan type compounds with excellent photo-promoting properties are described by the same Applicant in Italian patent 1,223,333.

The physical form and tendency towards crystallization of the above compounds creates serious limitations in the preparation of liquid compositions that are stable in the long term. In the present text, the term stable signifies stable as to crystallization.

In pure form or in the conditions shown in Italian patent 1,223,333, the above compounds are crystalline or vitreous solids that, once dissolved, show at very high concentrations (30% to 80%), a more or less marked tendency to crystallize.

Other solid photo-promoters also tend to crystallize when one wants to prepare concentrated solutions to be added to mixtures to be photo-polymerized, and as a consequence photo-promoter substance based compositions have to be prepared immediately prior to use, and cannot be stored, or marketed either.

C. The technical problem

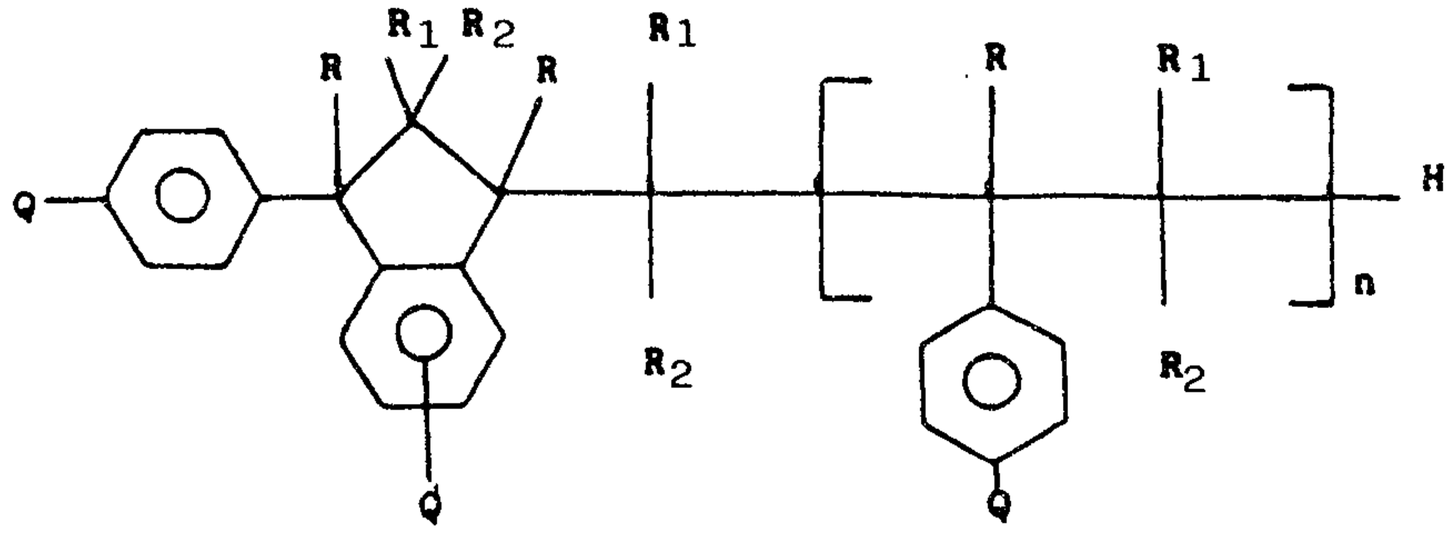
1-Phenylindan type photo-promoting substances are solids or vitreous solids, thus it is necessary to prepare solutions to be added to polymerization mixtures.

These solutions are not stable in the long-term as they tend to sediment, and are thus prepared immediately prior to use.

What is in fact required are long-term stable solutions that can be stored and marketed in a ready for use form, and are easy to dose and mix with photo-polymerization mixtures.

D. Detailed Description of the Invention

The present invention refers to stable liquid compositions containing between 25 and 75 parts by weight of at least one solvent chosen from the group consisting of inert diluents, reactive diluents, and active diluents, and between 25 and 75 parts by weight of at least one 1-phenyindan carbonyl derivative, whose structure is represented by the formula:



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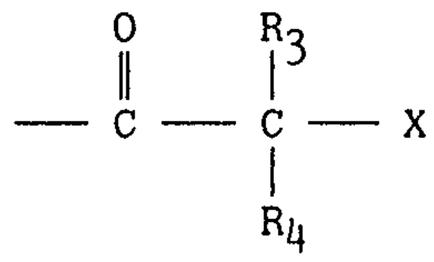
where:

n : from 0 to 1;

R, R_1, R_2 : the same or different, each independently represent H, C_1-C_3 alkyl;

Q : represents a group



in which:

R_3, R_4 the same or different, each can independently be:

- C_1-C_8 alkyl,
- together they can be a C_3-C_7 polyalkylene group,
- together they can coincide in an oxygen atom;

X : can be Cl, OH, OR in which R has the same meaning as before,

and to the process for their preparation and their use.

Favoured compositions contain between 30 and 70 parts by weight of derivatives of formula (I).

The term inert diluents signifies solvents such as toluene, xylene, methylene chloride, methylethyl ketone, and butyl acetate.

The term reactive diluents signifies monomers that are normally used in mixtures to be photo-polymerized, such as acrylic esters of glycols and polyols, and, possibly ethoxylated. As examples of reactive diluents, we mention tripropyleneglycol diacrylate, hexandiol diacrylate, trimethylol propane ethoxylate acrylate, N-vinyl pyrrolidone, and bisphenol-A-ethoxylate acrylate.

The term active diluents signifies photo-promoters such as, for example, alphahydroxy isobutyrrophenone, liquid benzophenones (eutectics of 2,4,6-trimethylbenzophenone and 4-methylbenzophenone), and diethoxyacetophenone.

The liquid compositions according to the invention preferrably contain tripropyleneglycol diacrylate as a reactive diluent.

In another favoured embodiment, the active diluent is a photo-promoter such as alphahydroxybutyrrophenone or the liquid eutectic composed of 80 parts 2,4,6-trimethylbenzophenone and 20 parts 4-methylbenzophenone.

The derivatives of formula (I) are known, and are described, together with their general use characteristics in Italian patent 1,223,333.

In the above mentioned patent application, the derivatives of formula (I) are prepared by simultaneously cyclizing and oligomerizing styrene type derivatives, and then introducing them into carbonyl group molecules.

Surprisingly, it has been found that under particular conditions during the simultaneous cyclizing and oligomerizing stage of the initial styrene compound, by functionalizing the resulting compound without separating it from the reaction medium, and diluting the reaction mixtures with inert, reactive, or active diluents, the resulting liquid compositions on the basis of 1-phenylindan carbonyl derivatives of formula (I) are highly stable.

The mixtures of 1-phenylindan carbonyl derivatives thus obtained contain between 70% and 90% by weight of dimers with a formula (I), where n=0, the remaining part being trimers with formula (I), where n=1.

According to a fundamental characteristic of the present invention, the stable liquid compounds that are the object of the invention are prepared by a process that includes the following essential stages:

A) Simultaneous cyclization and oligomerization of a styrene compound chosen from the group including styrene, alpha-methylstyrene, styrene alpha substituted by C_2-C_4 alkyls and diphenylethylene, in the presence of an acid catalyst and in the absence of solvents, carried out in two stages: a first stage carried out at a temperature of 55° to 80°C for 1 to 3 hours, and a second stage at 120°C for 1 to 3 hours;

B) Introduction of carbonyl groups by Friedel-Crafts acylation, as described in the previous patent application EP 161463, by treating the mixture of oligomers resulting from stage A, dissolved in a

solvent chosen from the group consisting of carbon sulphide, methylene chloride, dichloroethane, 1,1,1-trichloroethane, and chloro-fluoro-hydrocarbons , or mixtures of them, with a solution in the same solvent of a complex between a carboxylic acid chloride and a Lewis acid catalyst at a temperature between -20°C and +20°C, followed by hydrolysis, washing with water, and evaporation of the solvent.

C) Dilution of the resulting mixture of 1-phenylindan carbonyl derivatives by addition of at least one diluent chosen in the group consisting of inert diluents, reactive diluents, and active diluents.

The favoured acid catalysts for carrying out stage A of the process that is the object of the present invention are acid clays, ion exchange resins with sulphur groups in an acid form, and C_1-C_{18} -alkyl and C_6-C_{18} -aryl-sulphonic acids, among which those that are in an insoluble solid form are most favoured as they are easier to separate from the reaction mixture once oligomerization is completed.

The Lewis acid catalysts useful for stage B of the process according to the invention are, for example, $AlCl_3$, BF_3, $SnCl_4$, and $TiCl_4$.

The liquid compositions according to the present invention are efficient in promoting the photo-polymerization of unsaturated monomers and prepolymers just as the compositions prepared immediately prior to use by admixing the various components.

EXAMPLE 1

The Preparation of the mixture of indan-phenyl-hydroxyketones from alpha-methylstyrene.

A) Simultaneous Cyclization and Oligomerization in Two Stages

10 g of alpha-methylstyrene and 4.3 g of Amberlyst 15 (Rohm and Haass) were placed in a reactor with a bottom valve under stirring in a nitrogen atmosphere. The mixture was heated to 60°C, the temperature maintained at 60° ± 5°C, and 420 g of alpha-methylstyrene were added over a period of 1 hour. The temperature (60° ± 5°C) was maintained for a further hour, at the end of which the mixture was heated to 120°C (± 10°C), and held at that temperature for around 1 hour. The catalyst was separated from the base of the reactor by settling (in total, 4.3 g of Amberlyst 15 and 10 g of alpha- methylstyrene oligomers were separated, and recycled in the next process).

B) Introduction of Carbonyl Groups

The mixture of oligomers (1) from stage A was diluted with 913 g methylene chloride. The resulting mixture was cooled to 20°C, and 813 g of alpha-bromo-isobutyrrylbromide were added.

493 g of anhydrous aluminium chloride were slowly added (without exceeding 20°C). The mixture was then heated to 40°C and held at that temperature for 3 hours.

The reaction mass was then poured into 1.8 l of water, and once it had been completely dissolved by the addition of 640 g methylene chloride, the organic phase was separated from the aqueous phase,

treated with 520 g of aqueous 50% solution of sodium hydroxide, and then heated to the boiling point for around two hours.

The aqueous phase was then separated, and once the water had been removed and the organic phase had been clarified by filtering, the solvent was removed by vacuum distillation (50 mmHg) at a temperature of up to 60°C.

A mixture of 685 g of hydroxyketone oligomers (2) was thus obtained, ready for dilution in the most suitable solvent.

C) Dilution

294 g of tripropyleneglycol diacrylate were then added, directly in the reactor, to the functionalized mixture of oligomers thus obtained.

The mixture was stirred until a homogenous mixture was obtained, and then poured into a container where it was left to cool to room temperature.

The resulting product was a viscous, clear, stable liquid that could be stored for months (at least 6).

EXAMPLE 2

The chemical physical properties and the efficiency during application of the liquid composition obtained as described in Example 1 (composition a) were evaluated, as were those of a comparative liquid composition (composition b) obtained starting with alphamethylstyrene under conditions similar to those in Example 1, with the exception of the following aspects: Stage A was carried out in a single phase at 120°C; the product obtained from

stages A and B was isolated before the successive stage; the dilution as described in stage C was carried out immediately prior to use.

The tests to evaluate the efficiency during the application of compositions a and b were conducted using the following resin formulation (all parts are by weight):

Polyurethane acrylate

Photomer 6250 - 90 parts (containing 25% tripropyleneglycol diacrylate)

N-vinylpyrrolidone - 10 parts

Composition a or b - 4 parts

The chemical physical properties and the results of the efficiency tests are shown in table 1.

Descriptions of the application tests are given in the notes at the foot of Table 1.

Table 1

	Composition a	Composition b
Appearance:	clear liquid	
Brookfield RVT viscosity 20rpm (Pa.s):	5-10	8-15
Specific gravity at 20°C (H_2O = 1):	1.09	1.09
Cross-linking rate[1] (m/min):	24	25
Cross-linked film hardness[2] (sec):	127	129
Yellow index		
- after cross-linking (YI)[3]:	17.8	18.2

- after 12 hours[3]:	15.0	15.4
- after 10 days aging[4]:	27.9	27.9
Resistance to MEK[5]		
(double rubs after 10 m/min)	>300	>300
Stability[6]		
- Non seeded at 20°C:	>3000	500 ap.
50°C:	>1000	100
- Seeded at 20°C:	>2000	250
50°C:	> 250	20

NOTES:

1 Evaluating cross-linking rate

The photo-polymerizable mixtures were spread on a card in a thickness of 50 µm, and subjected to cross-linked using a Hanovia 6512-A-431 lamp at 80 W/cm at a distance of 10 cm. The criterion used for evaluation was the maximum speed (in m/min) at which the film was no longer sticky.

2 Evaluating the Hardness of the Reticulated Films

The photo-polymerizable mixtures were spread on glass in a thickness of 100 µm and cross-linked under the same conditions as in test 1 at a speed of 10 m/min.

The hardness was measured according to DIN standard 53157 (Koenig pendulum, in seconds).

3 Evaluating the Yellow Index

The photo-polymerizable mixtures were spread 100 µm thick on a card and cross-linked as in test 1. The yellow index (Y1) was

measured using apparatus as per ASTM standard D 1925.

4 Evaluating the Resistance to Aging

The photo-polymerizable mixtures were spread and reticulated as in test 1, and the resulting films were subjected to accelerated aging in a Weather-O-Meter. The yellow index (Y1) was measured according to the ASTM standard D 1925 after 10 days aging.

5 Evaluating the Resistance to MEK

The photo-polymerizable mixtures were cross-linked as in test 1, and the resulting films were subjected to double rubbing with a cotton pad soaked in methylethylketone (MEK). Resistance to MEK was expressed as the number of double rubs required before a film showed visible signs of damage.

6 Stability

Stability, expressed as the time in hours before a quantity of sediment equal to 15% of the total mass appears, was determined on liquid composition samples a and b, maintained at the temperature shown on the Table.

From the point of view of efficiency during application, no particular differences between compositions a and b were detected. As far as their chemical/physical properties are concerned, composition a showed stability to crystallization, both when seeded and unseeded (crystalline germ), considerably higher than the composition b.

EXAMPLE 3

A liquid composition was prepared as described in example 1, and

evaluated as described in example 2 after being stored for 6 months. It then showed chemical/physical properties and efficiency during application that were entirely analogous to those of the composition in Example 1.

EXAMPLE 4

70 parts of hydroxyketone oligomers (2) were prepared as described in example 1 a) and b), and were diluted as described in example 1 c) with 30 parts alphahydroxybutyrrophenone. The composition thus obtained was a clear liquid that was long-term stable[1], and had the following properties:

Table 2

Appearance:	clear liquid
Brookfield viscosity, 20 rpm, 20°C:	15 - 30 Pa.s
Specific gravity at 20°C (H_2O = 1):	1.1

Viscosity variation[2] in the time

(hours at 20°C)	Brookfield RVT viscosity 20 rpm, 20°C
200	19500
400	20500
600	19500
1000	18250
1250	18000

NOTE 1: No sediment was observed in the composition kept at 20°C for 1250 hours.

NOTE 2: Viscosity values were measured on the basis of the elapsed

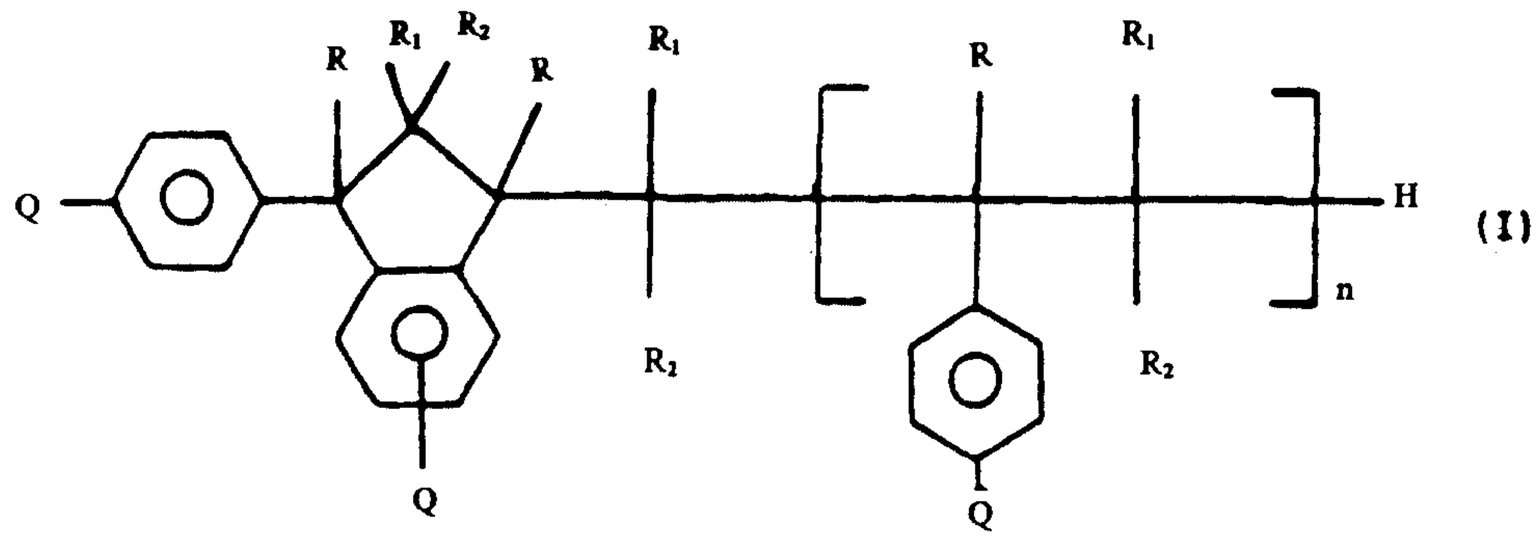
time at 20°C.

EXAMPLE 5

70 parts of hydroxyketone oligomers (2) prepared as described in example 1 a) and b), were diluted as described in example 1 c) with 30 parts of an eutectic liquid composed of 80 parts 2,4,6-trimethylbenzophenone and 20 parts 4-methylbenzophenone. The composition thus obtained was a clear liquid that was stable for over 12 months at 20°C (appearance = clear liquid; Brookfield RVT viscosity at 20 rpm, 20°C = 1.5 - 3.5 Pa.s; Density at 20°C (H_2O = 1) = 1.07; Pouring point = -5°C).

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A stable liquid composition containing between 25 and 75 parts by weight of at least one solvent chosen from the group consisting of xylene, methylethyl ketone, butyl acetate, an optionally ethoxylated acrylic ester of a glycol or of a polyol, N-vinyl pyrrolidone, alphahydroxy isobutyrrophenone, a liquid benzophenone and diethoxyacetophenone, and containing between 25 and 75 parts by weight of at least one 1-phenylindan carbonyl derivative, whose structure is represented by the formula:



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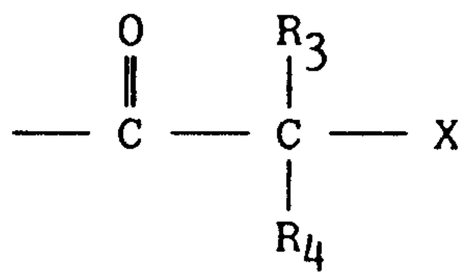
wherein:

n is from 0 to 1;

R, R_1, R_2 are the same or different, and each independently represents H or C_1-C_3 alkyl;

Q represents a group



in which R_3 and R_4 are the same or different, and either each is independently a C_1-C_8 alkyl group; or

together they can be a C_3-C_7 polyalkylene group; or

together they can coincide in an oxygen atom; and

X is Cl, OH, or OR in which R has the same meaning as defined above before.

2. A stable liquid composition according to claim 1, containing between 30 and 70 parts by weight of the derivatives of formula (I).

3. A stable liquid composition according to claim 1, wherein the 1-phenylindan carbonyl derivative contains between 70% and 90% by weight of dimers of formula (I), where n=0, the remaining part being trimers of formula (I), where n=1.

4. A stable liquid composition according to claim 1, 2 or 3, wherein the acrylic ester is selected from the group consisting of tripropyleneglycol diacrylate, hexandiol diacrylate, trimethylol propane ethoxylated acrylate, and bisphenol-A-ethoxylated acrylate.

5. A stable liquid composition according to claim 4, wherein the acrylic ester is tripropyleneglycol diacrylate.

6. A stable liquid composition according to any one of claims 1 to 5, wherein the solvent is alphahydroxybutyrrophenone.

7. A stable liquid composition according to any one of claims 1 to 6, wherein the liquid benzophenone is an eutectic liquid mixture of 80 parts 2,4,6-trimethylbenzophenone and 20 parts 4-methylbenzophenone.

8. Process for the preparation of a liquid composition as defined in claim 1, the process comprising the steps of:

A) simultaneous cyclization and oligomerization of a styrene compound chosen from the group consisting of styrene, alpha-methylstyrene, and styrene alpha-substituted by C_2-C_4 alkyls and diphenylethylene, in the presence of an acid catalyst and in the absence of solvents, carried out in two stages:

a first stage carried out at a temperature of 55° to 80°C for 1 to 3 hours; and

a second stage at 120°C for 1 to 3 hours;

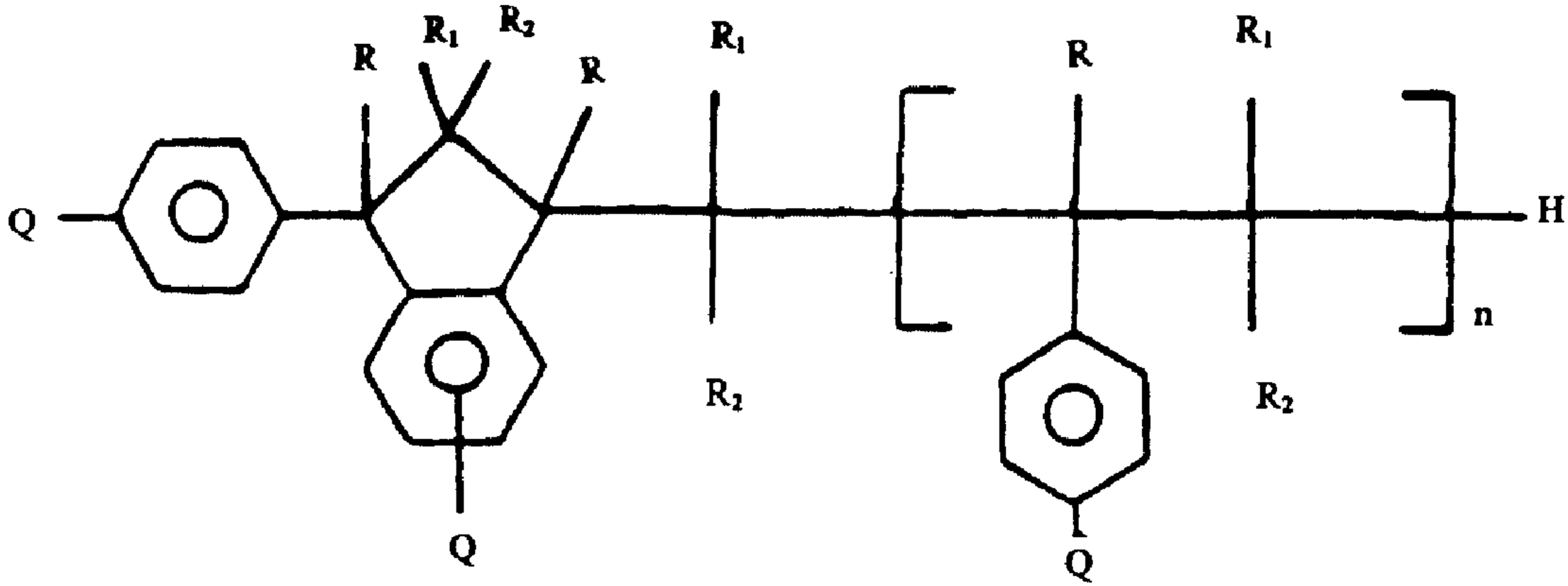
B) introduction of carbonyl groups carried out by Friedel-Crafts acylation, by treating the mixture of oligomers resulting from stage A), dissolved in a solvent

chosen from the group consisting of carbon sulphide, methylene chloride, dichloroethane, 1,1,1-trichloroethane, and chloro-fluoro hydrocarbons, or mixtures thereof, with a solution in the same solvent of a complex between a carboxylic acid chloride and a Lewis acid catalyst at a temperature of between -20°C and +20°C, followed by hydrolysis, washing with water, and the evaporation of the solvent;

C) dilution of the resulting mixture of 1-phenylindan carbonyl derivatives by addition of at least one solvent chosen from the group consisting of xylene, methylethyl ketone, butyl acetate, an optionally ethoxylated acrylic ester of a glycol or of a polyol, N-vinyl pyrrolidone, alphahydroxy isobutyrrophenone, a liquid benzophenone and diethoxyacetophenone.

9. A process according to claim 8, wherein the acid catalyst used to carry out stage A) is chosen from the group consisting of acid clays, ion exchange resins with sulphonic groups in acid form, and C_1-C_{18} -alkyl-sulphonic and C_6-C_{18} -aryl-sulphonic acids.

10. A process according to claim 8 or 9, wherein the acid catalyst used in stage A) is in solid form.



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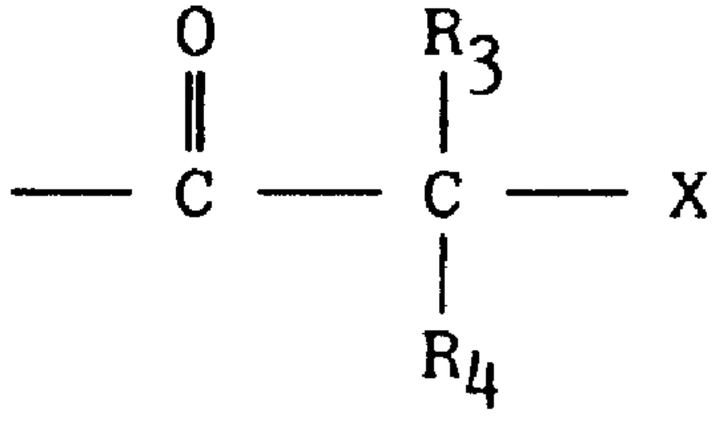

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