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(71) Demandeur/Applicant:
OLEOTEK INC., CA

(72) Inventeur/Inventor:
BERTHIAUME, DAVID, CA

(74) Agent: ROBIC

(54) Titre : REFRIGERANTS DIELECTRIQUES POUR UTILISATION DANS DES APPAREILS ELECTRIQUES

(54) Title: DIELECTRIC COOLANTS FOR USE IN ELECTRICAL EQUIPMENT



DIELECTRIC COOLANTS FOR USE IN ELECTRICAL EQUIPMENT

FIELD OF THE INVENTION

5 The present invention relates to a synthetic insulating fluid for use as a dielectric and cooling medium in power and distribution electrical apparatus, such as transformers, oil bath breakers and attendant equipment.

BRIEF DESCRIPTION OF THE PRIOR ART

10 Oleochemistry is a broad science which finds application in multiple fields, such as lubricants, paints, plastics, fuels, cosmetics, food, and pharmaceutical products. Oleochemistry further finds an application in the field of transmission and distribution of electrical power, and particularly for transformers in which important quantities of dielectric coolant are used.

15 The dielectric coolants employed in the electric transformers are mostly of mineral and petrochemical origin. However, some electric transformers using vegetable oil based dielectric coolants are newly presented on the American and European markets. These new coolants have the advantage of being efficient, biodegradable and non-toxic according to the American regulation. Until today, these coolants are mostly used for installations located nearby ecologically sensitive sites, such as rivers and other natural places, or indoor locations, such as commercial
20 buildings and towers.

25 Vegetable oil based dielectric coolants are efficient and environmentally friendly as they are biodegradable and non-toxic. However, they are limited in their utilisation because of their relatively high temperature operating range (usually limited to operating temperatures higher than -20°C). This value, which corresponds to the coolant's pour point, is acceptable for the majority of the American states, but is insufficient for the cold climate found in northern countries where the temperature often drops below the general -20°C pour point. Thus, the pour point of standard dielectric coolants for cold climates is of about -40°C . The lowering of the pour point is limited by the nature of these coolants.

There are known dielectric coolants in the art such as those sold by ABB inc (Biotemp[®]), by Cargill (BioTrans[®]) and by Cooper Power Systems (Envirotemp[®]). These products are made of purified and treated vegetable oil combined with conservative agents and other additives. These oils are biodegradable, non-toxic and have increased flash points. However, as mentioned above, these oils have a pour point unsuitable for use in electrical equipments located in at least -40°C climates and usually require the presence of additives when intended for operation temperatures around -20°C.

US patent no. 6.726.857 discloses dielectric coolants comprising relatively pure blends of compounds selected from the group consisting of aromatic hydrocarbons, polyalphaolefins, polyol esters, and natural vegetable oils, along with additives to improve pour point, increase stability and reduce oxidation rate. However, this US patent does not seem to disclose the use of a mixture of only polyol esters as dielectric coolants.

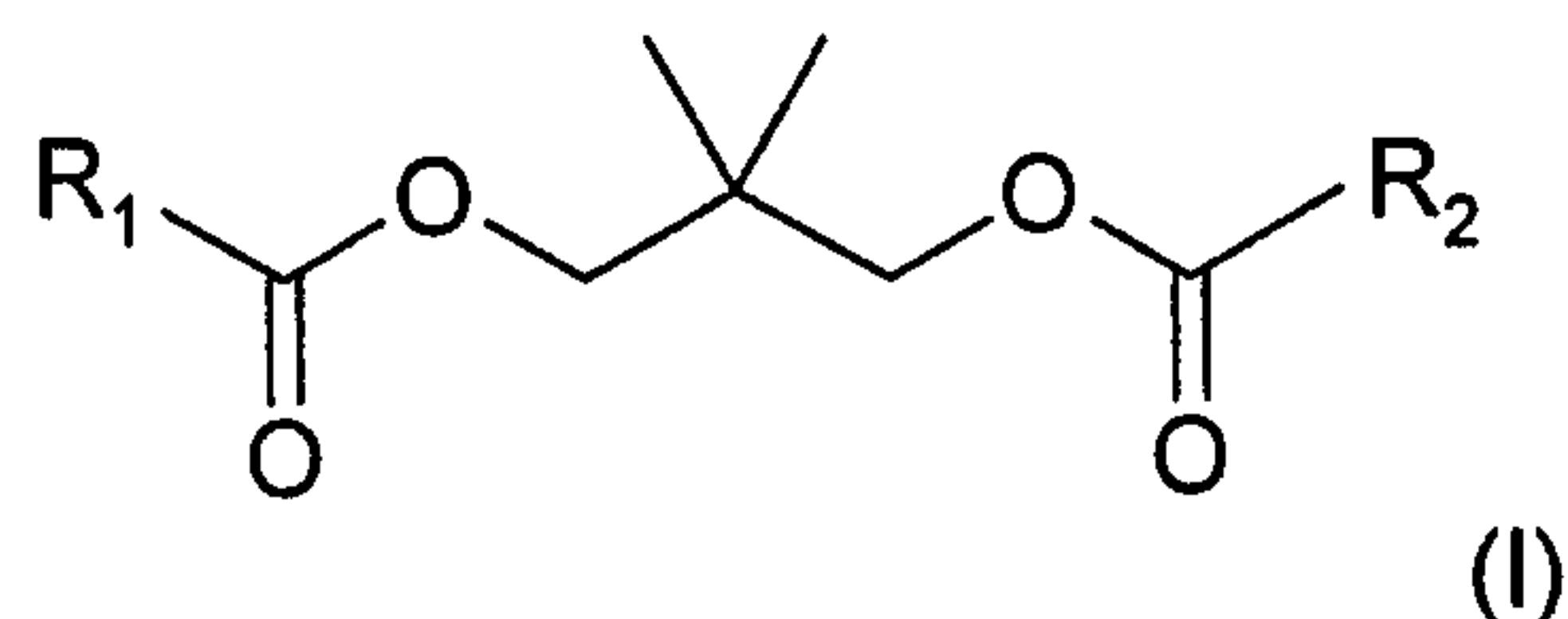
Therefore, there is a constant need for innovating new dielectric coolants that are biodegradable, non-toxic, and efficient in cold climates, especially meeting operating temperatures colder than -40°C.

SUMMARY

An object of the invention concerns a dielectric coolant having a pour point of at least about -40°C for use in power distribution equipment for cold climates.

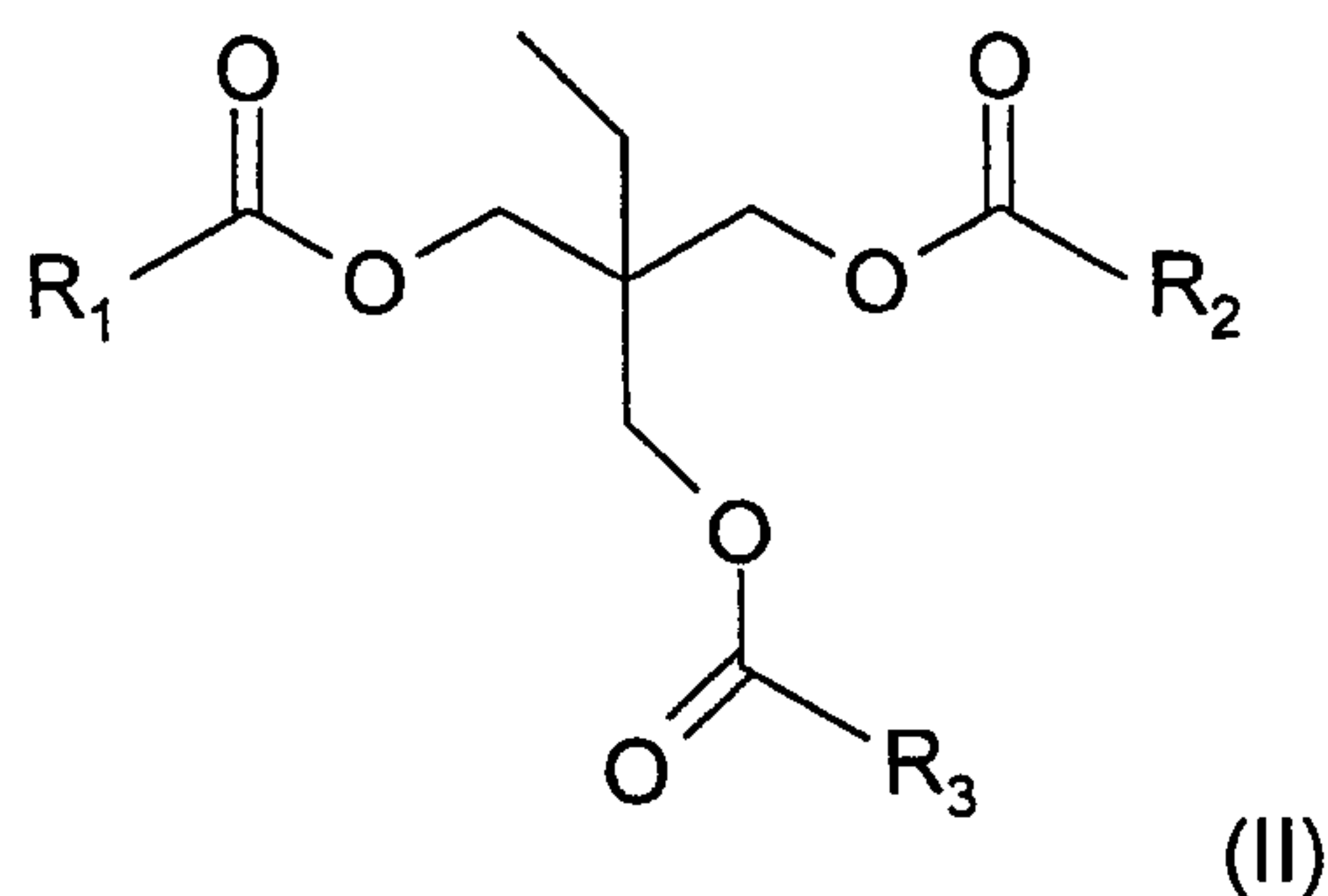
More specifically, such an object is achieved by providing a dielectric coolant having at least a pour point of about -40°C, and comprising a mixture of more than one compound chosen from the following:

- a polyol ester of formula I:



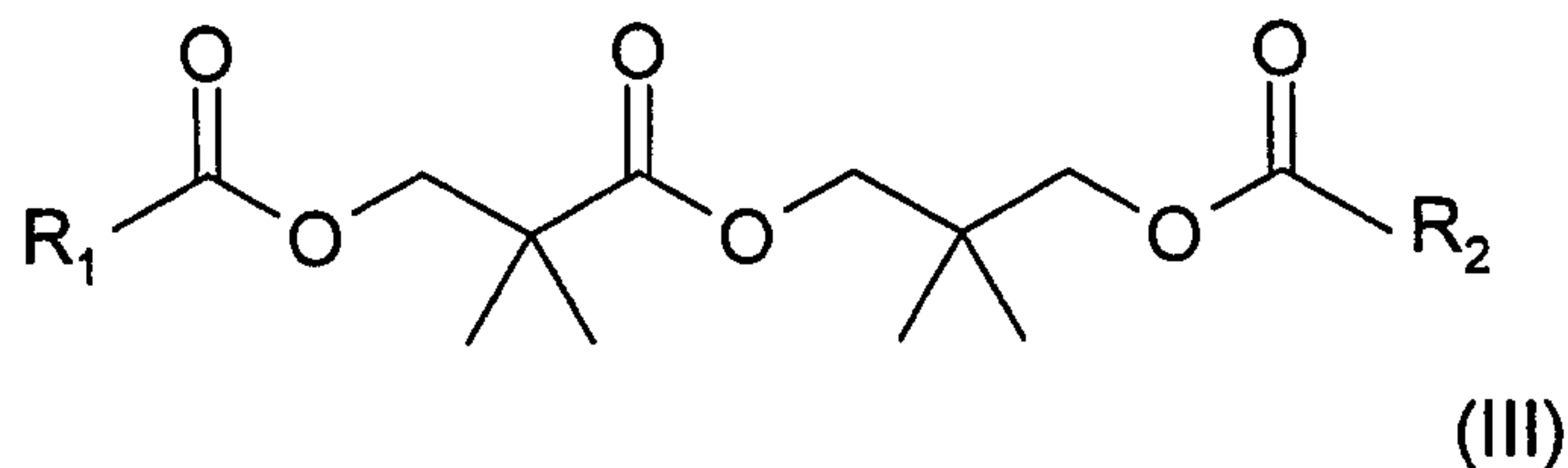
wherein R_1 and R_2 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} ; and/or

- a polyol ester of formula II:



5 wherein R_1 , R_2 and R_3 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} .

Another object of the invention is to provide a dielectric coolant having at least a pour point of about -40°C , and comprising a hydroxypivalic acid neopentylglycol ester (HPN ester) of formula III:



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wherein R_1 and R_2 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} .

The present invention has the advantage of providing dielectric coolants having at least one of the following characteristics:

15

- no need for pour point depressant additives;
- more resistant to hydrolysis and oxidation;
- non-toxic;

- biodegradable;
- pour point up to -100°C; and
- flash point of at least 200°C.

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DETAILED DESCRIPTION OF THE INVENTION

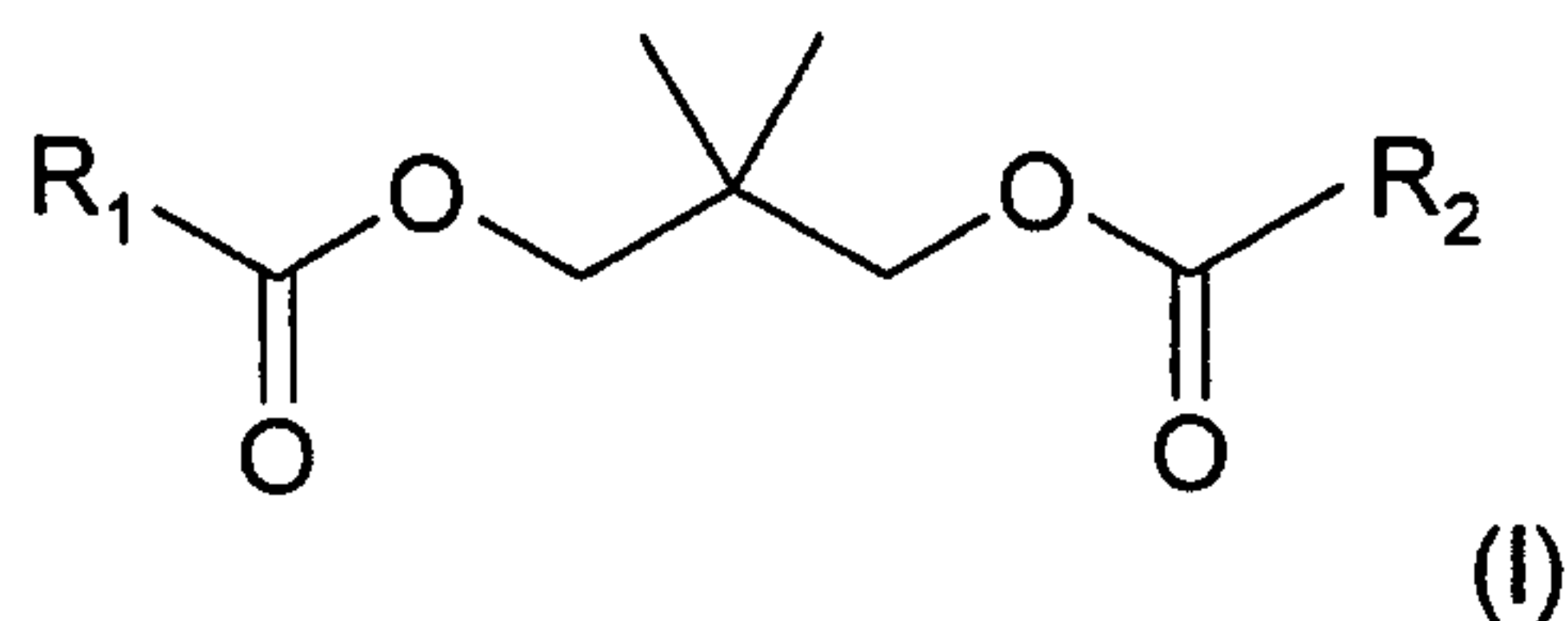
The inventor has surprisingly found that the use of a mixture of polyol esters, preferably combined with a hydroxypivalic acid neopentylglycol ester (HPN ester) offers an efficient fluid as a dielectric coolant useful in power distribution equipment, such as transformers. It will be understood that a transformer is a device that transfers electric power from one circuit to another by electrical magnetic means. Transformers are used extensively in the transmission of electrical power, both at the generating end and the user's end of the power distribution system. A distribution transformer is one that receives electrical power at a first voltage and delivers it at a second, lower voltage.

A dielectric coolant of the present invention should possess at least one of the following characteristics. It should transfer heat effectively, have an appropriate dielectric strength, and/or should not possess ingredients harmful to the environment. As mentioned above, it has been surprisingly found that a HPN ester or a mixture of polyol esters and combination thereof satisfy both the requirements for suitability as dielectric coolant in cold climates and the requirements relating to environmental compatibility.

Polyol esters result from the chemical combination of polyalcohol compounds with organic acids containing a variety of alkyl groups.

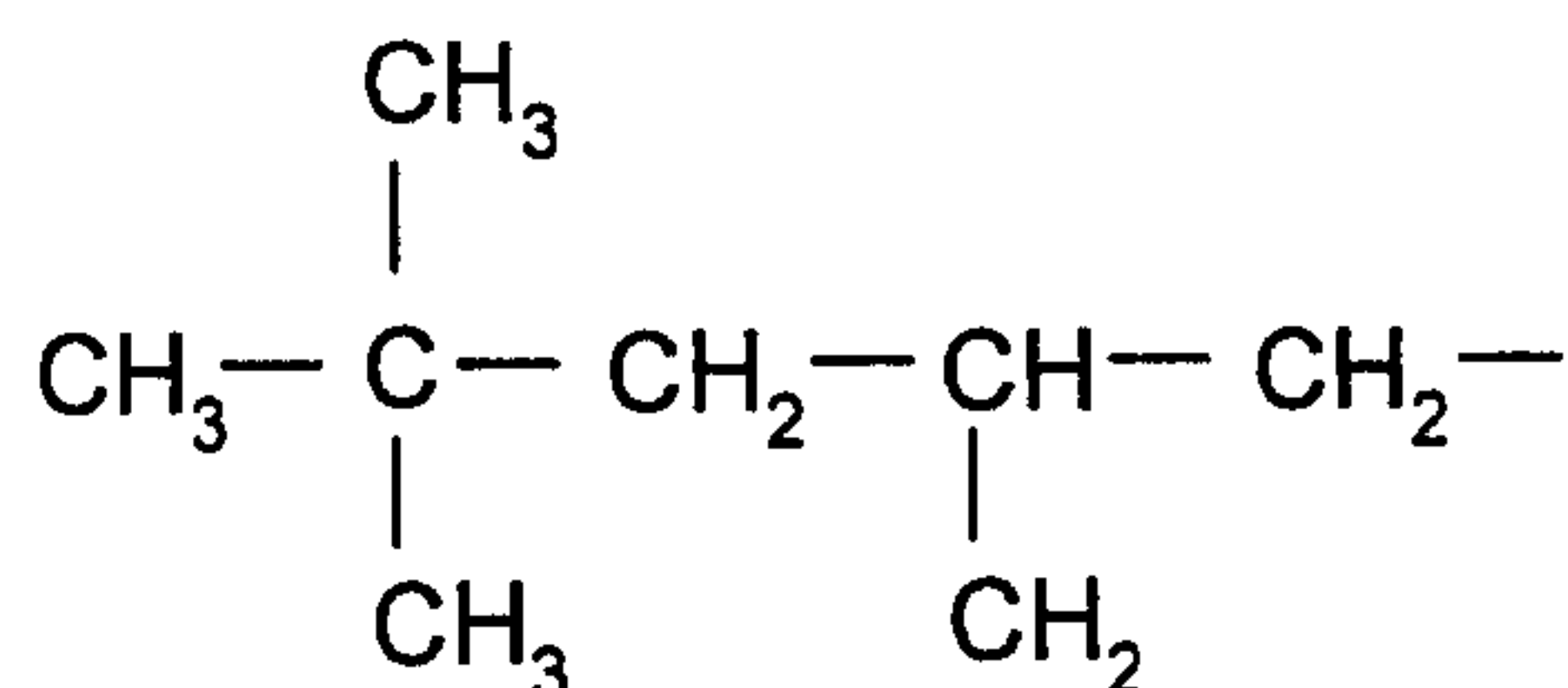
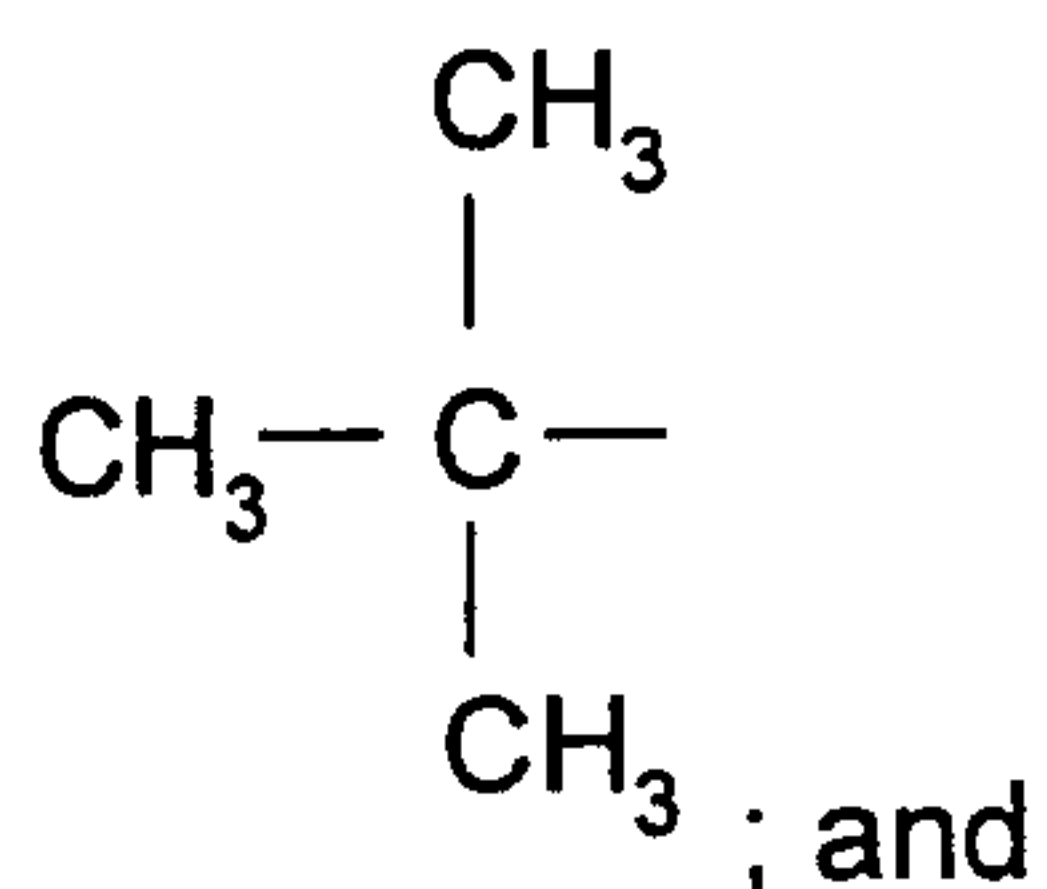
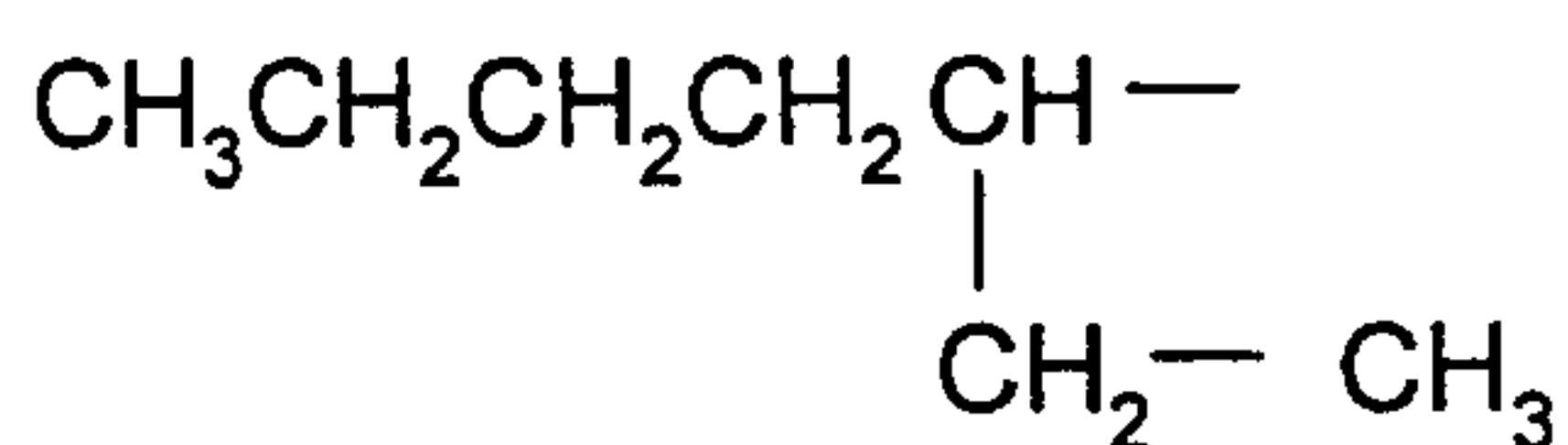
The first preferred polyol ester is neopentyl glycol having the following formula:

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wherein R_1 and R_2 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} . R_1 and R_2 preferably present chains of natural or synthetic origin that offer a good level of biodegradability. Even more preferably, R_1 and R_2 present chains obtainable from a biological source such as from vegetable or animal oils.

According to the present invention, R_1 and R_2 can be selected from the group consisting of :

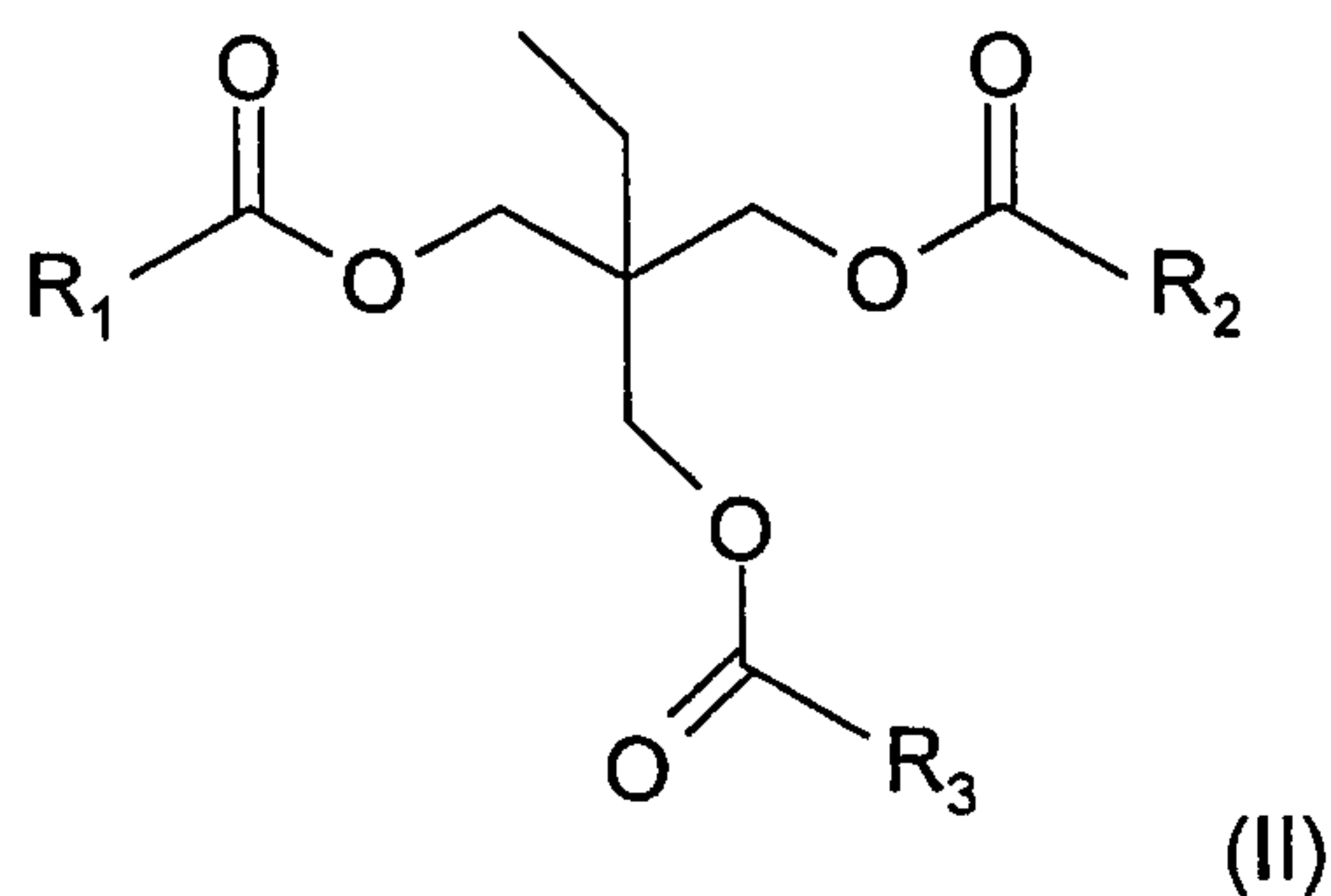


According to a preferred embodiment, R_1 and R_2 are:





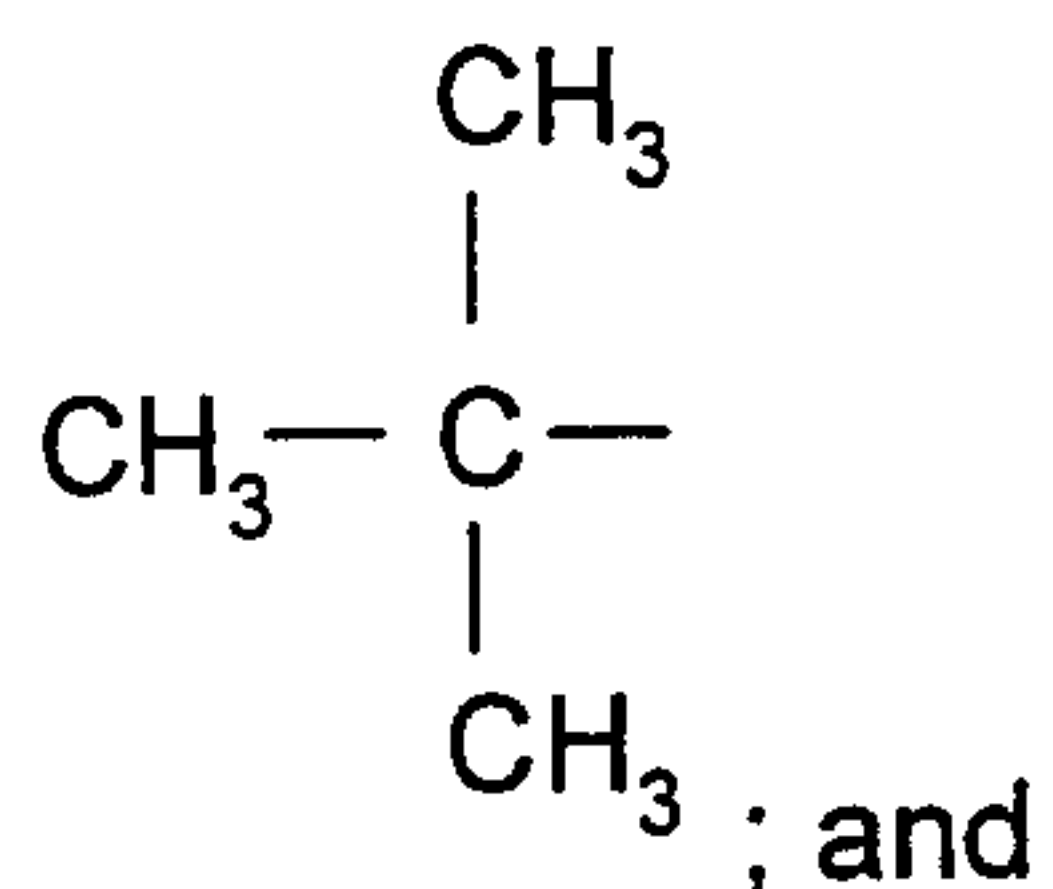
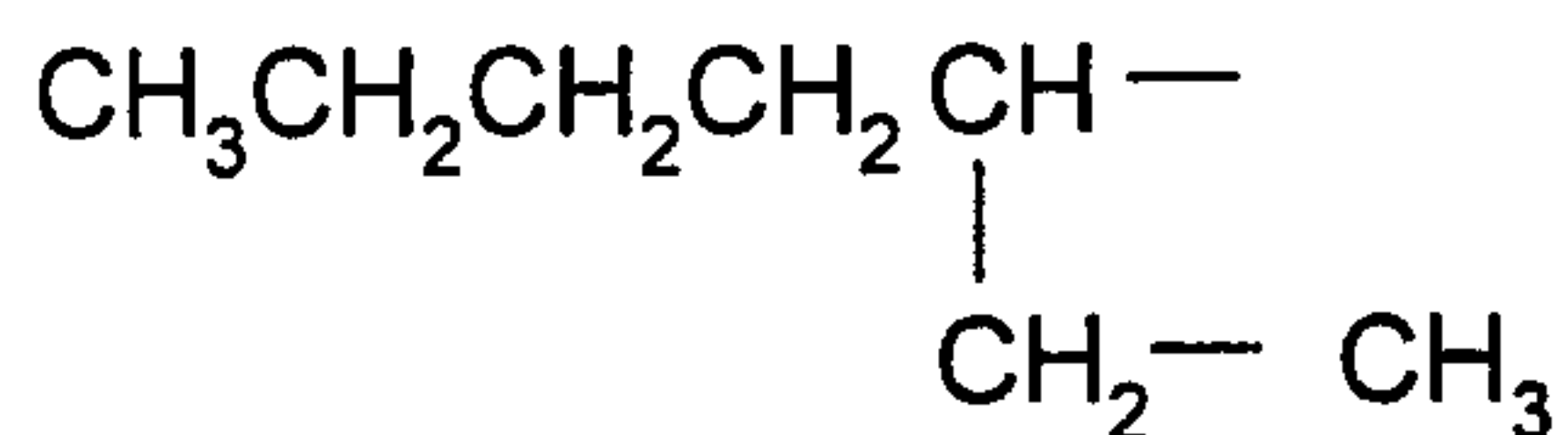
The second preferred polyol ester is trimethylolpropane having the following formula:

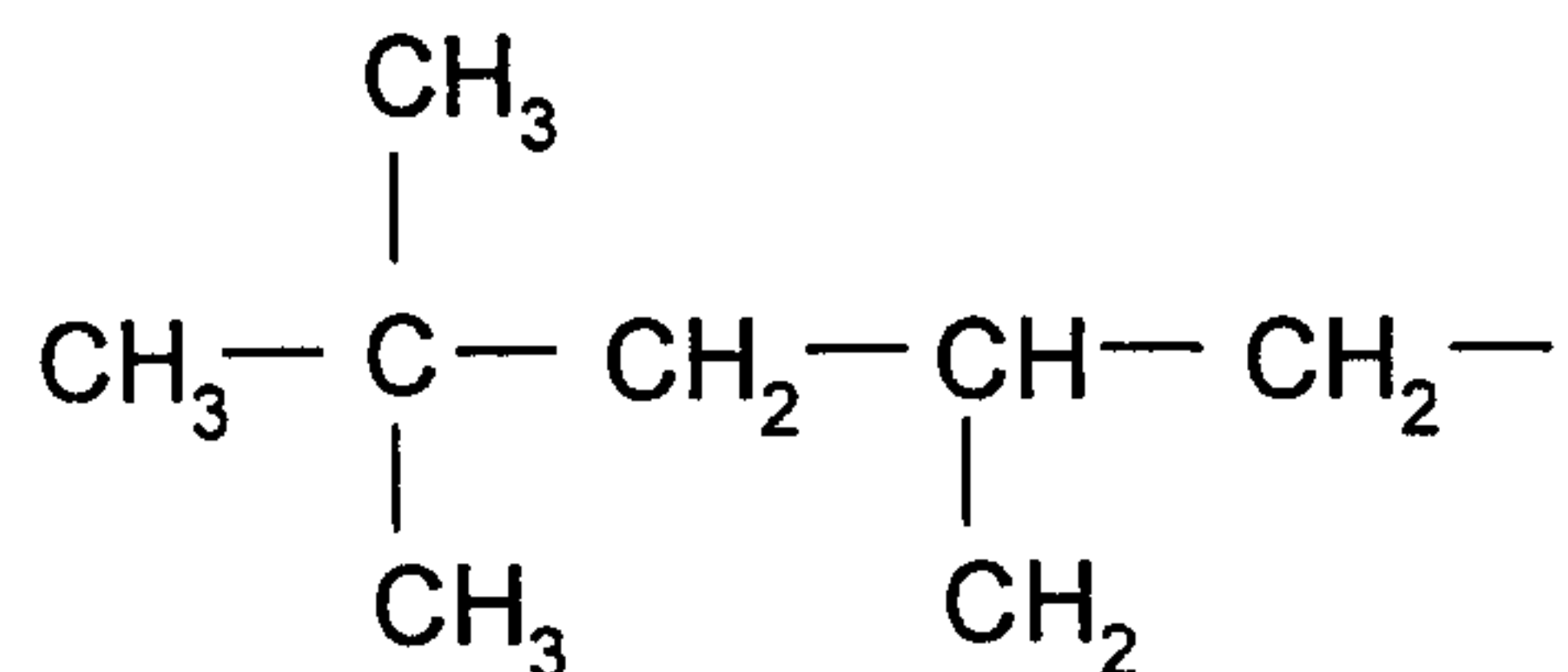


5 wherein R_1 , R_2 and R_3 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} .

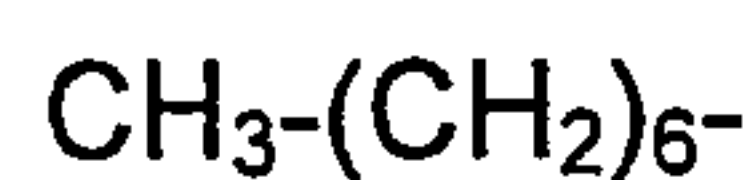
R_1 , R_2 and R_3 preferably present chains of natural or synthetic origin that offer a good level of biodegradability. Even more preferably, R_1 , R_2 and R_3 present chains obtainable from a biological source such as from vegetable or animal oils.

10 Accordingly, R_1 , R_2 and R_3 can be selected from the group consisting of



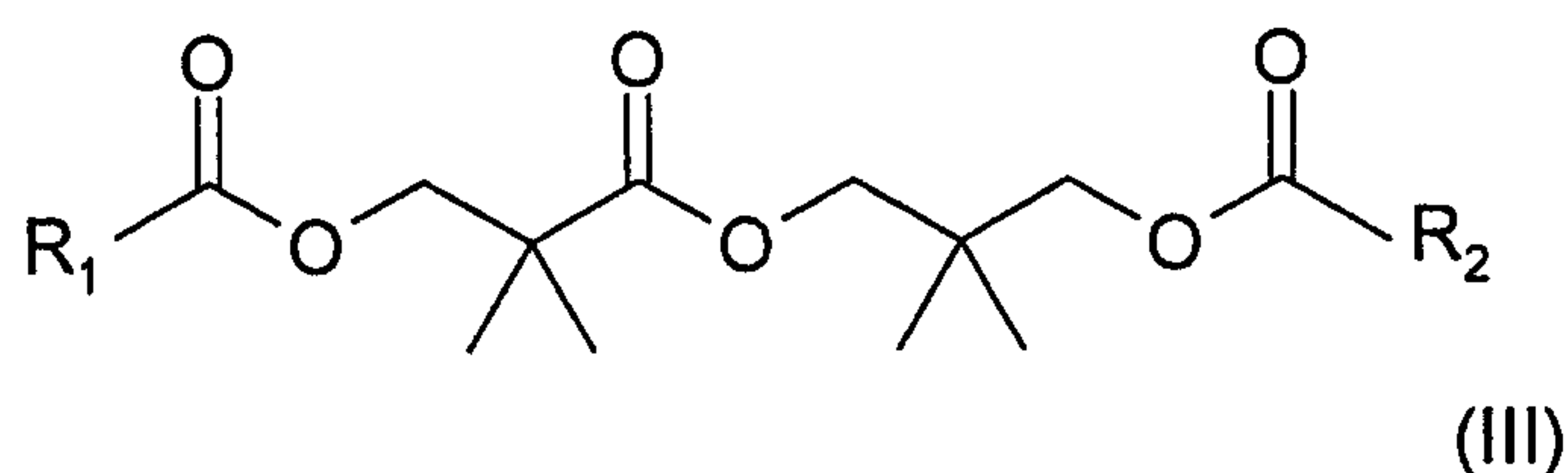


According to a preferred embodiment, R_1 , R_2 and R_3 are:



5 It will be understood that a dielectric coolant contemplated by the invention comprises a mixture of more than one of the above defined polyol esters, and thus encompasses a mixture of polyol esters of formula I and of formula II, but also a mixture of different polyol esters of formula I or II.

According to a preferred embodiment, the dielectric coolant of the invention further comprises a hydroxypivalic acid neopentylglycol ester (HPN ester) of the following formula:



wherein R_1 and R_2 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} . Preferably, R_1 and R_2 have the same meaning as defined above.

According to a preferred embodiment, R₁ and R₂ are CH₃-(CH₂)₆-.

As it will be understood by one skilled in the art, the pour point of a dielectric coolant affects its usefulness particularly with regards to electrical equipment in cold climates. In this connection, a dielectric coolant of the present invention has a pour

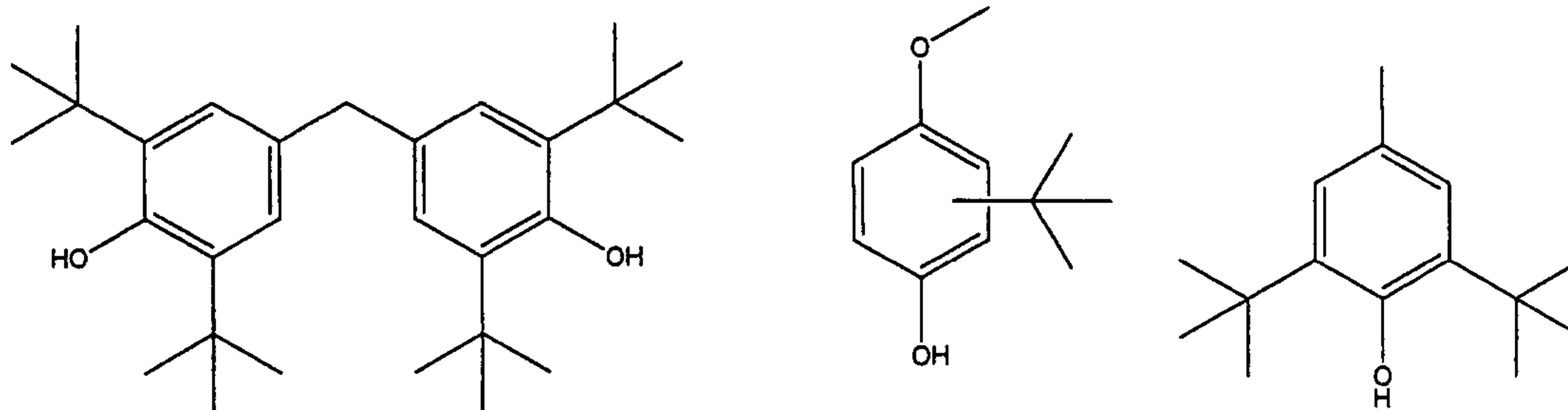
point of at least about -40°C , more preferably of at least about -60°C , and even more preferably of at least about -100°C .

According to another preferred embodiment, a dielectric coolant of the present invention has a flash point of at least about 200°C . It will be understood that the flash point is the lowest temperature at which a flame will set light to the vapour of the oil or its degradation product. It represents a qualification test and is employed on a pre-industrial scale.

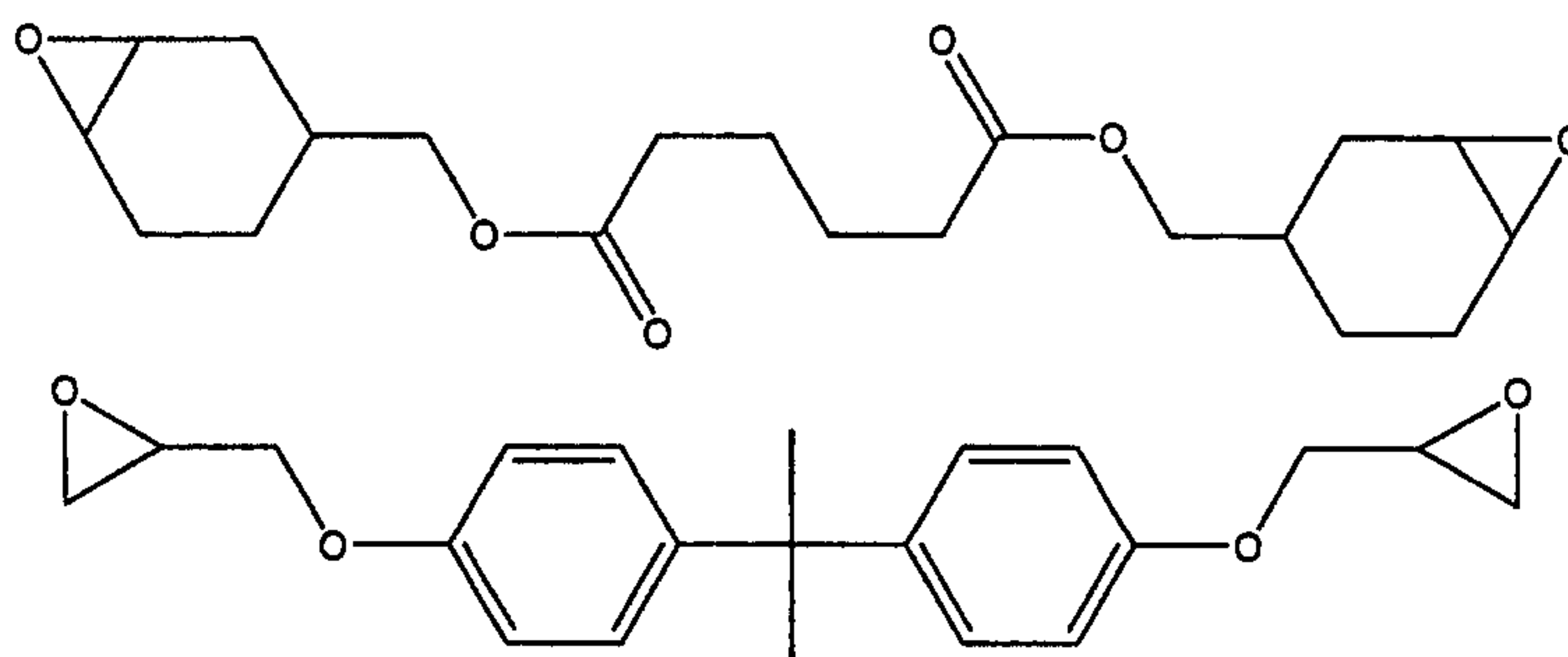
By "about", it is meant that the value of said pour point or flash point can vary within a certain range depending on the margin of error of the method used to evaluate such pour point or flash point.

According to the present invention, additives can be further added to the dielectric coolant described above in relatively small amount. These additives are selected from the group consisting of antioxidants, stabilizers, and biocides.

Preferred antioxidants include, but are not limited to, phenolic antioxidants, with 2,6-di-tert-butyl-paracresol (DBPC). BHA and BHT being particularly preferred antioxidants, having the formula:



Preferred stabilizers include, but are not limited to, epoxide additives. Examples of epoxide additives used to prevent degradation of the esters are:



There exists a very wide variety of biocid compounds in the art. Preferred biocides include, but are not limited to, pyrithione derivatives, halogenated pyridine derivatives, triazole derivatives, and tetrahydrofuran derivatives.

- 5 The present invention will be more readily understood by referring to the following examples. These examples are illustrative of the wide range of applicability of the present invention and are not intended to limit its scope. Modifications and variations can be made therein without departing from the spirit and scope of the invention. Although any method and material similar or equivalent to those described
- 10 herein can be used in the practice for testing of the present invention, the preferred methods and materials are described.

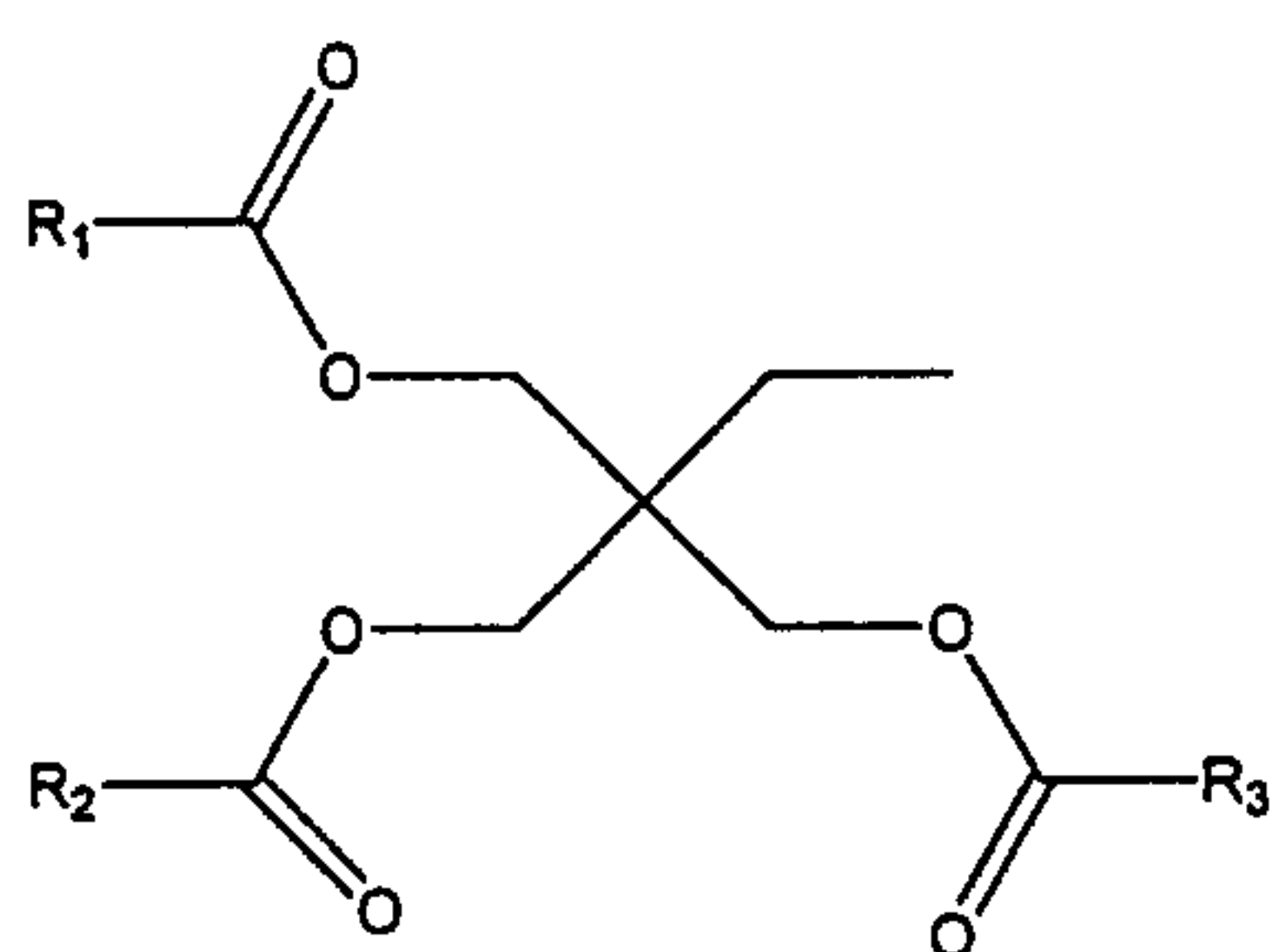
EXAMPLES

Physical and chemical properties of preferred dielectric coolants

- 15 The polyol esters and HPN esters mixtures of the present invention were obtained by esterifying the appropriate polyol compound or mixture with the appropriate carboxylic acid compound or mixture with an acid catalyst in a Dean Stark apparatus and/or formulation of separate batches thereof.
- 20 The polyol esters and HPN esters mixtures of the present invention could also be obtained by esterifying the appropriate polyol compound or mixture with the appropriate carboxylic acid compound or mixture with a determined amount of hydroxipivalic acid with an acid catalyst in a Dean Stark apparatus and/or formulation of separate batches thereof.

EXAMPLE 1

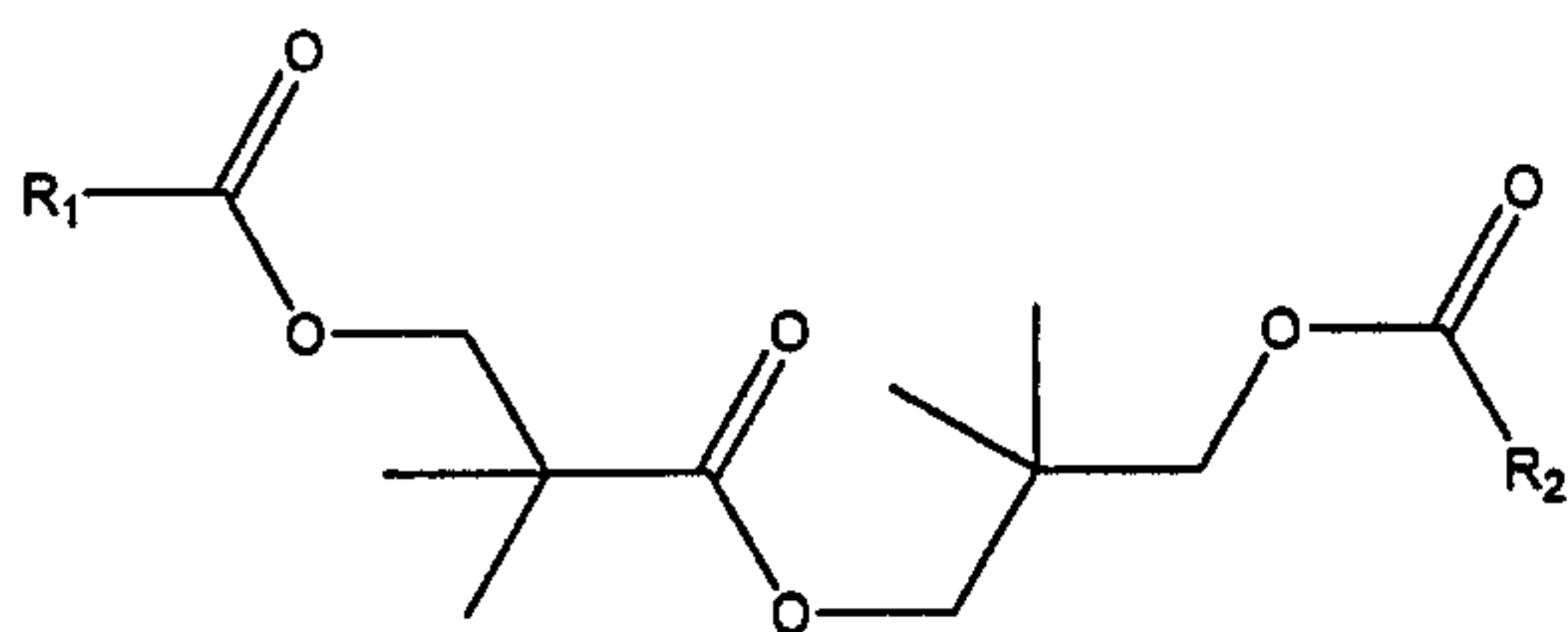
Caprylic acid (667,3 g; 4,53 mol) and trimethylolpropane (202,3 g; 1,46 mol) are placed in a Dean Stark apparatus with toluene (solvent; 3,2 liters) and p-toluenesulfonic acid (catalyst; 14,2 g; 73 mmol) and heated at reflux under mechanical agitation for 5 hours. The solvent is then evaporated and the remaining oil is washed with a sodium carbonate solution and water to remove catalyst and unreacted caprylic acid.



Where R_1 , R_2 and R_3 are $\text{CH}_3\text{-(CH}_2\text{)}_6\text{-}$.

EXAMPLE 2

Caprylic acid, oleic acid, and HPN are placed in a Dean Stark apparatus with toluene and benzenesulfonic acid (catalyst) and heated at reflux under mechanical agitation for 6 hours. The solvent is then evaporated and the remaining oil is quickly washed with a diluted sodium hydroxide solution and brine.

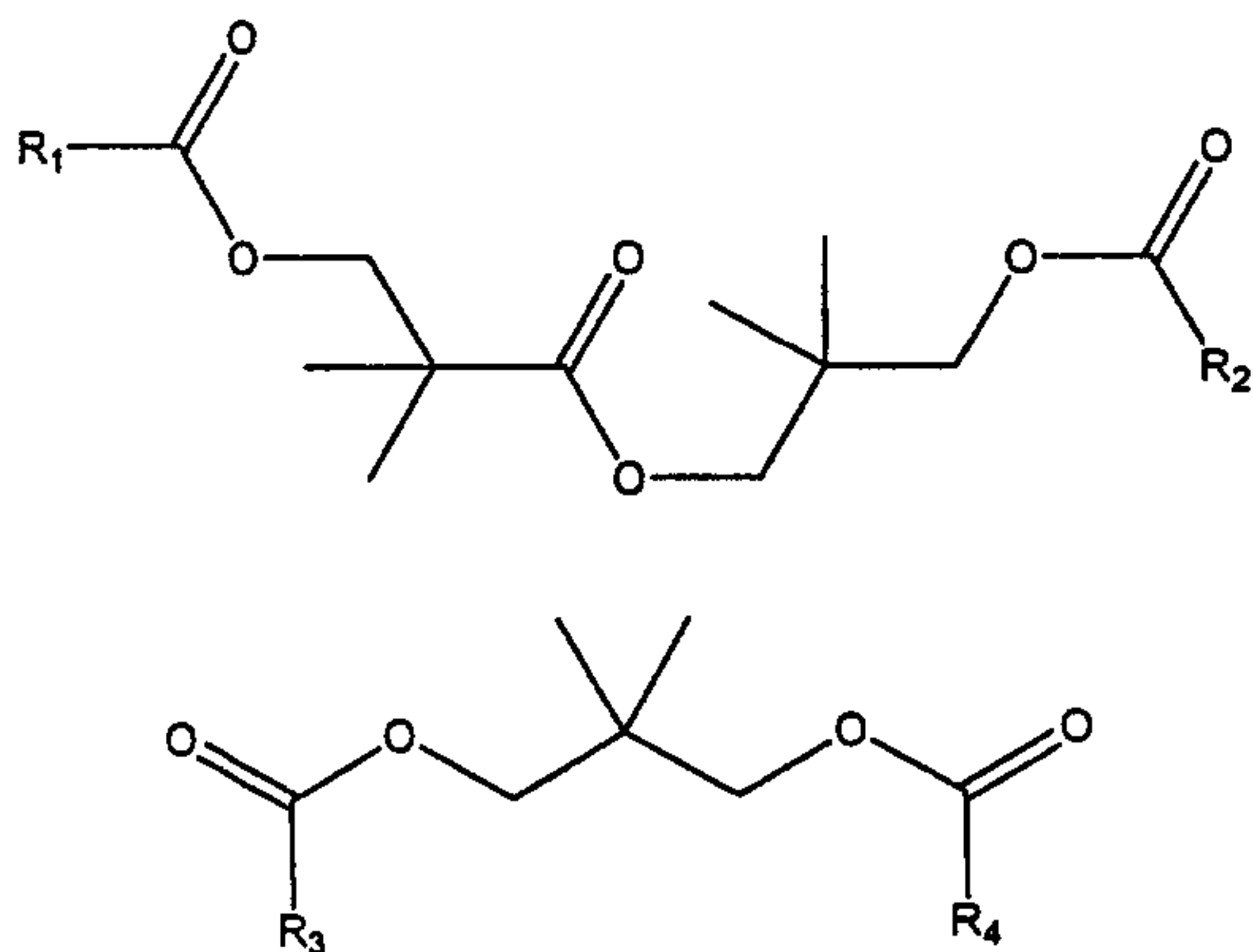


Where R_1 and R_2 independantly are $\text{CH}_3\text{-(CH}_2\text{)}_6\text{-}$ or $\text{CH}_3\text{-(CH}_2\text{)}_7\text{-CH=CH-(CH}_2\text{)}_7\text{-}$.

EXAMPLE 3

Caprylic acid, oleic acid, HPN and neopentylglycol are placed in a Dean Stark apparatus with toluene and benzenesulfonic acid (catalyst) and heated at reflux under mechanical agitation for 6 hours. The solvent is then evaporated and the resulting ester mix is quickly washed with a diluted sodium hydroxide solution and brine.

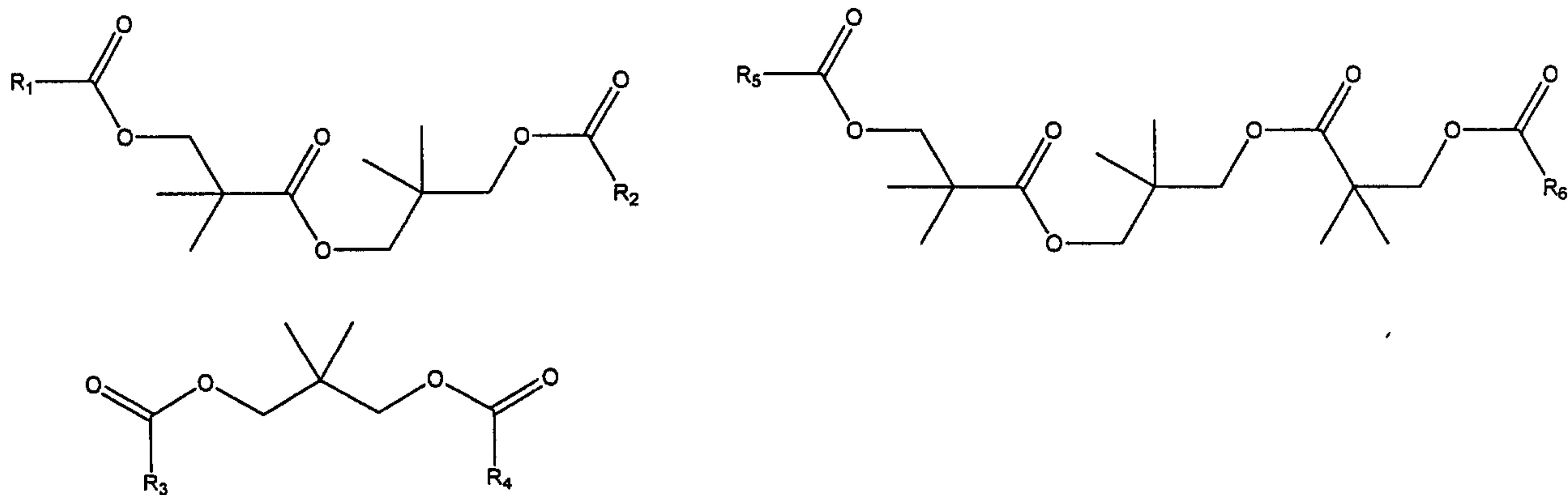
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Where R₁, R₂, R₃, and R₄ independantly are CH₃-(CH₂)₆- or CH₃-(CH₂)₇-CH=CH-(CH₂)₇-.

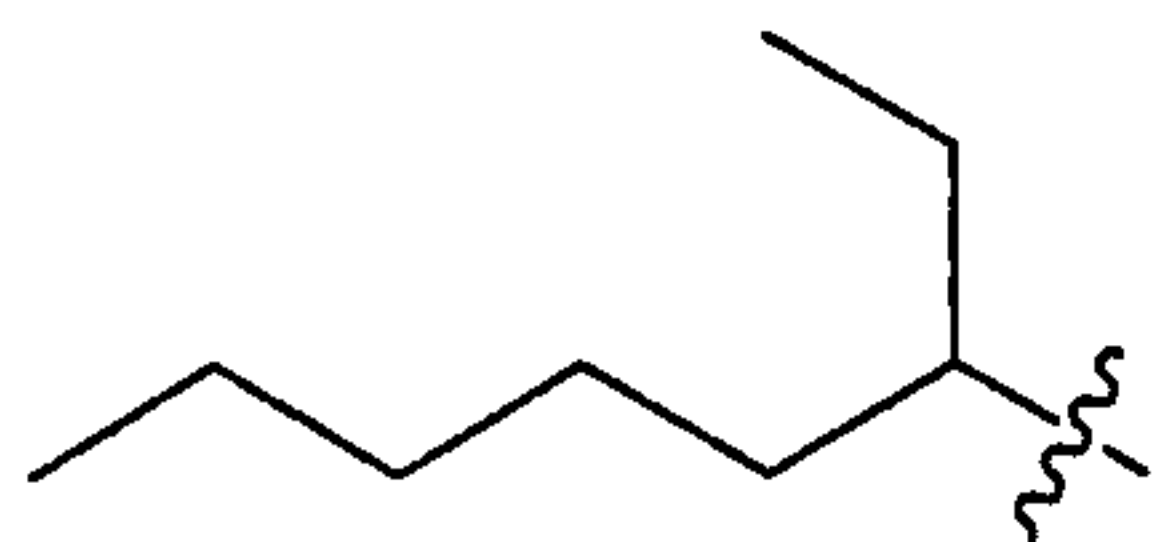
5 EXAMPLE 4

2-Ethylhexanoic acid, neopentyl glycol and hydroxypivalic acid are placed in a Dean Stark apparatus with toluene and p-toluenesulfonic acid (catalyst) and heated at reflux under mechanical agitation for 6 hours. The solvent is then evaporated and the remaining ester mix is washed with a sodium carbonate solution and water.



10

Where R₁, R₂, R₃, R₄, R₅ and R₆ are independently:



CH₃-(CH₂)₄-CH(2-ethyl)-.

EXAMPLE 5

75 weight percent of neopentyl glycol dicaprylate is blended with 25 weight percent of HPN-dioleate. To the resulting blend is added 0.5 weight percent of an oxidation inhibitor such as 2,6-di-tert-butyl-paracresol (DBPC).

EXAMPLE 6

To the blend obtained in EXAMPLE 5 is added an epoxide stabilizer.

- 10 Physical and chemical properties of preferred dielectric coolants of the invention shown in Table 1 were determined by the following methods:
- oxidative stability : method EN 14112
 - kinematic viscosity : method ASTM D445
 - flash and fire points : method ASTM D92
 - 15 - pour point : method ASTM D97.

TABLE 1: PHYSICAL AND CHEMICAL PROPERTIES OF PREFERRED DIELECTRIC COOLANTS CONSTITUENTS

Preferred compound of the invention	Oxidative stability* (h)	Viscosity 40°C (cP)	Viscosity 0°C (cP)	Flash point (°C)	Fire point (°C)	Relative density (g/cm ³ at 24°C)	Pour point (°C)
TMP-tricaprylate	9,85	20,6	84,6	238	282	0,948	-63
TMP-trioleate	0,7	42,0	194,7	-	-	0,912	-45
NPG-dicaprylate	6,6	7,6	25,8	200	224	0,917	-66
HPN-dicaprylate	7,94	14,3	63,6	238	260	0,953	-54

* Oxidative stability : at 130°C and 10L/h airflow

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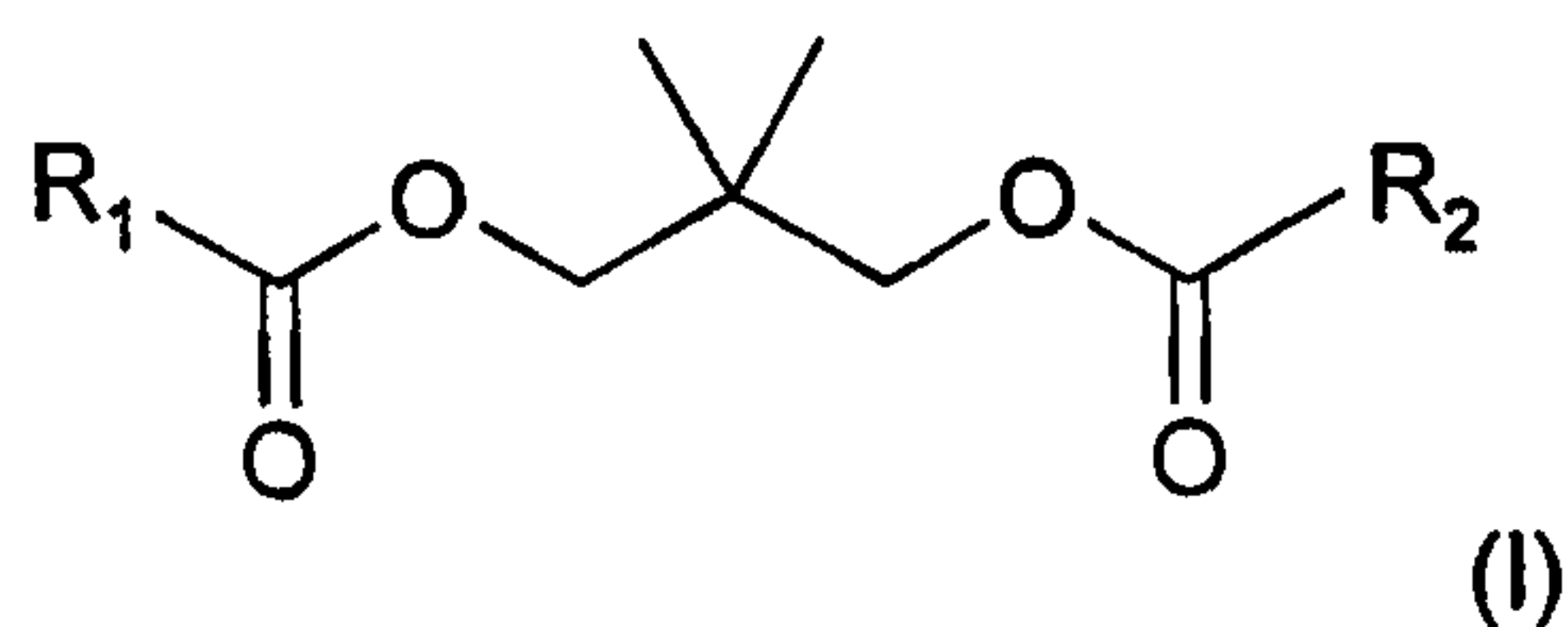
TABLE 2: PHYSICAL PROPERTIES OF PREFERRED DIELECTRIC COOLANTS MIXTURES

Test	Formulation	Pour point °C	Cloud point °C
1	25% HPN-dicaprylate and 75% NPG-dicaprylate	< -75	< -60
2	50% HPN-dicaprylate and 50% NPG-dicaprylate	< -74	< -60
3	75% HPN-dicaprylate and 25% NPG dicaprylate	-67	-24
4	25% HPN-dicaprylate and 75% TMP-tricaprylate	-61	-45
5	50% HPN-dicaprylate and 50% TMP-tricaprylate	-61	< -60
6	75% HPN-dicaprylate and 25% TMP-tricaprylate	-58	< -60
7	25% NPG-dicaprylate and 75% TMP-tricaprylate	-64	-39
8	50% NPG-dicaprylate and 50% TMP-tricaprylate	-72	-42
9	25% NPG-dicaprylate and 75% TMP-tricaprylate	< -72	-45

CLAIMS:

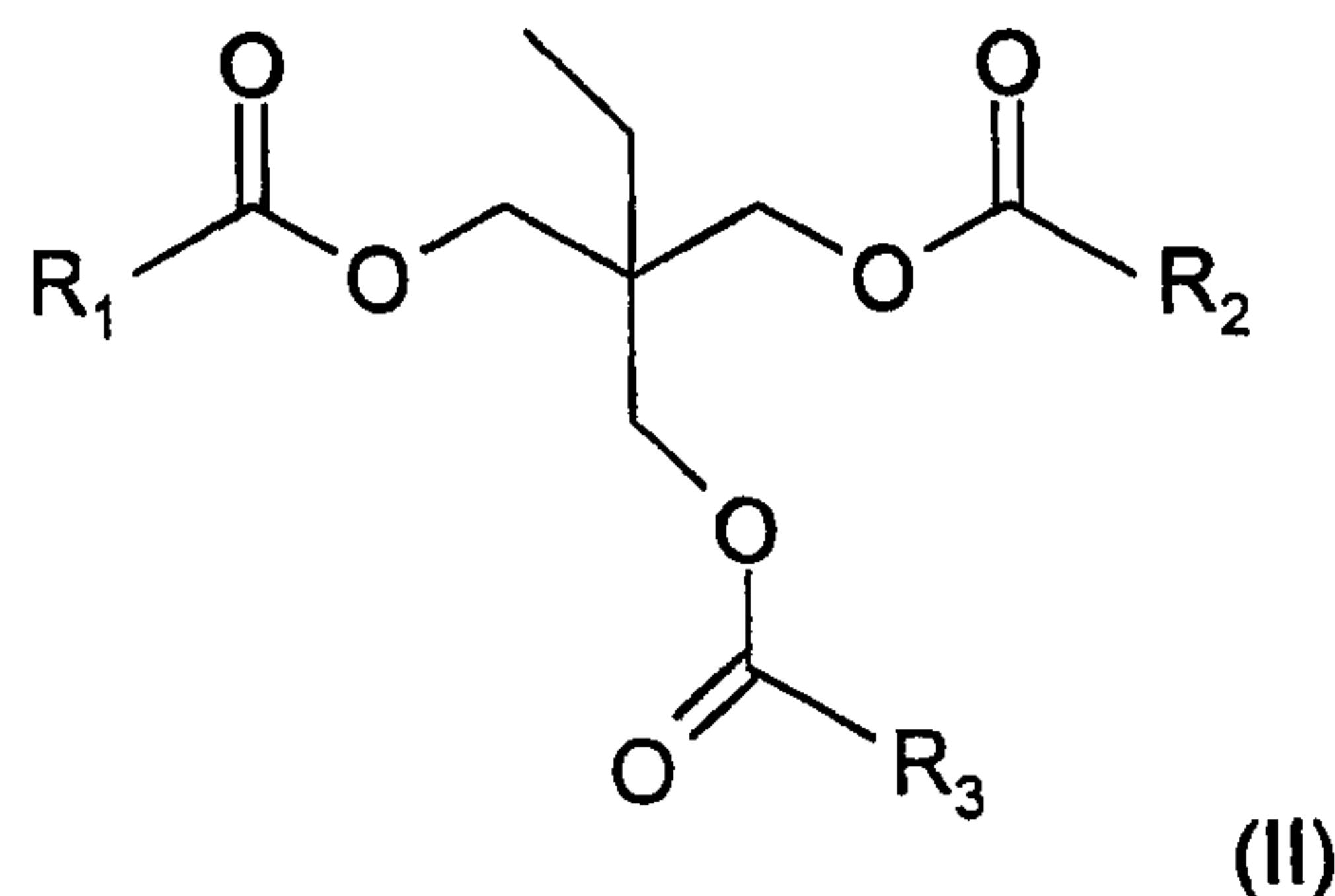
1. A dielectric coolant having at least a pour point of about -40°C , and comprising a mixture of more than one compound chosen from the following:

- polyol esters of formula I:



wherein R_1 and R_2 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} ; and/or

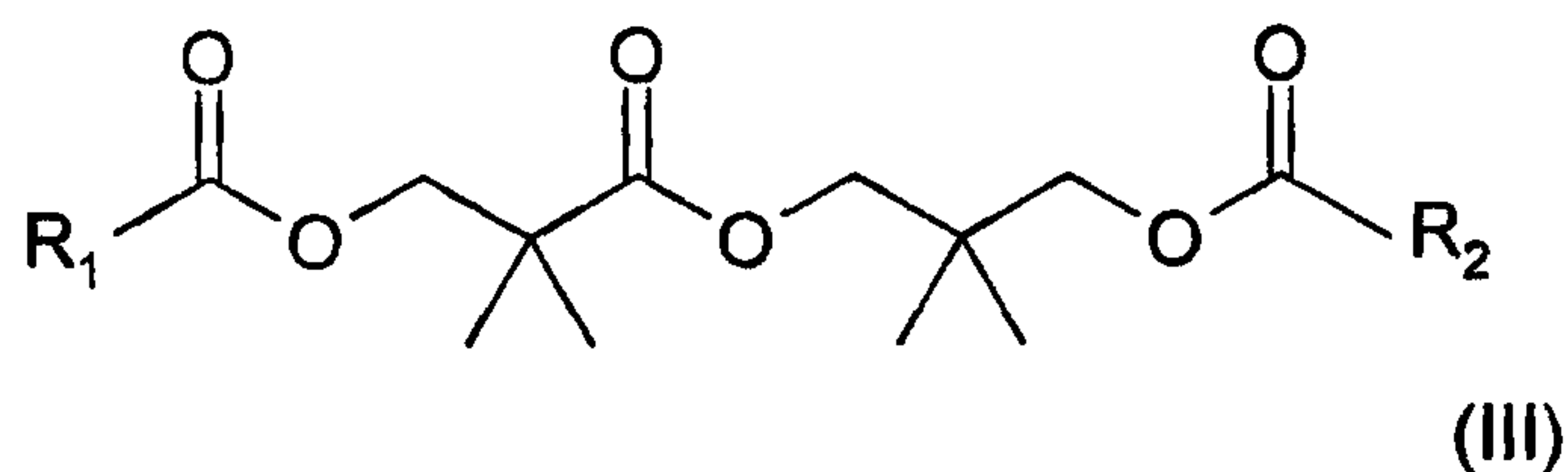
- polyol esters of formula II:



wherein R_1 , R_2 and R_3 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} .

2. The dielectric coolant of claim 1, wherein R_1 , R_2 and R_3 independantly are $\text{CH}_3-(\text{CH}_2)_6-$ or $\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-$.
3. The dielectric coolant of claim 1 or 2, wherein it further comprises a hydroxypivalic acid neopentylglycol ester (HPN ester) of formula III:

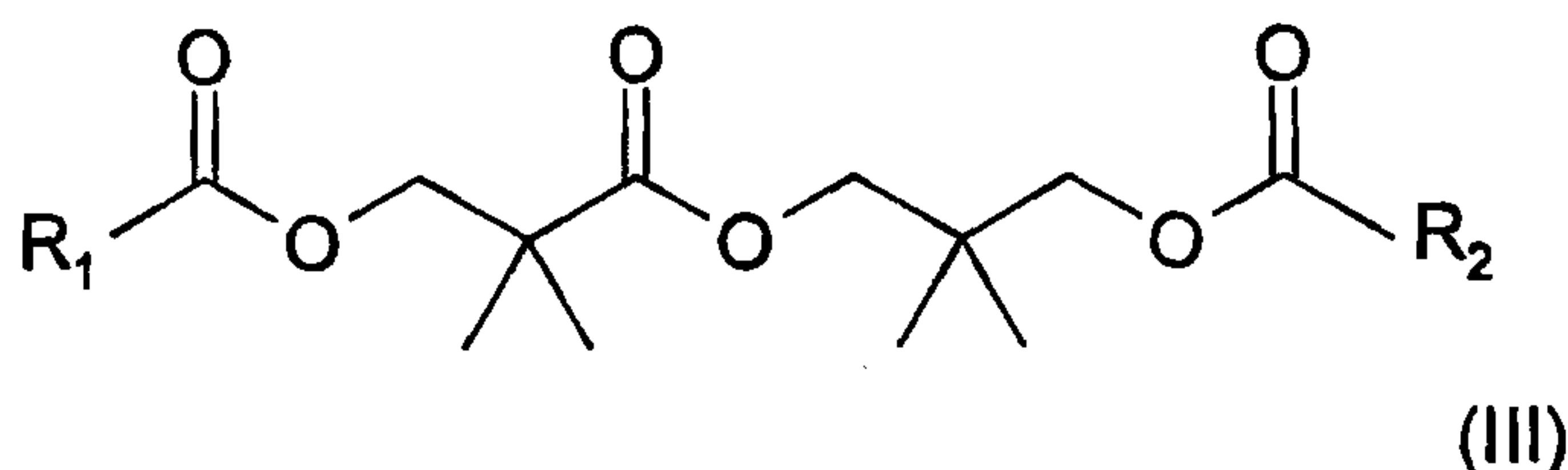
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wherein R_1 and R_2 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} .

4. The dielectric coolant of claim 3, wherein R_1 and R_2 are $CH_3-(CH_2)_6-$.

5. A dielectric coolant having at least a pour point of about $-40^\circ C$, and comprising a hydroxypivalic acid neopentylglycol ester (HPN ester) of formula III:



wherein R_1 and R_2 are the same or different and are selected from branched or unbranched alkyl groups with carbon chain lengths of C_5 to C_{22} .

6. The dielectric coolant of claim 5, wherein R_1 and R_2 are $CH_3-(CH_2)_6-$.

7. The dielectric coolant according to any one of claims 1 to 6, having a pour point ranging from about $-60^\circ C$ to about $-100^\circ C$.

8. The dielectric coolant according to any one of claims 1 to 7, further comprising an additive selected from the group consisting of an antioxidant and a stabilizer.

9. The dielectric coolant according to any one of claims 1 to 8, having a flash point of about $200^\circ C$ or higher.