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(71) Demandeur/Applicant:
CPH INNOVATIONS CORPORATION, US

(72) Inventeurs/Inventors:
O'ROURKE, STEPHEN E., US;
STEFANISIN, KIMBERLY L., US;
WENWORTH, GARY, US;
SHAH, URVIL B., US;
VU, YEN, US

(74) Agent: SMART & BIGGAR

(54) Titre : ESTERS DE DIMERATE ET DE TRIMERATE DE FAIBLE POLARITE UTILISES COMME PLASTIFIANTS
POUR DES COMPOSITES DE POLYMER/ELASTOMERE THERMOPLASTIQUES
(54) Title: LOW POLARITY DIMERATE AND TRIMERATE ESTERS AS PLASTICIZERS FOR THERMOPLASTIC
POLYMER/ELASTOMER COMPOSITES

(57) Abrégé/Abstract:

A thermoplastic polymer/elastomer composite composition including one or more thermoplastic polymers, a natural or synthetic rubber, and a long chain cyclic dimerate ester and/or long chain cyclic trimerate ester plasticizer.

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(74) Agent: LAWRENCE, Andrew, M.; Marshall, Gerstein & Borun, Suite 6300, 233 South Wacker Drive, Sears Tower, Chicago, IL 60606-6357 (US).

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(71) Applicant: THE C.P. HALL COMPANY [US/US]; 311 South Wacker Drive, Suite 4700, Chicago, IL 60606-6622 (US).

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(72) Inventors: O'ROURKE, Stephen, E.; 1847 Marne Road, Bolingbrook, IL 60490 (US). STEFANISIN, Kimberly, L.; 4867 Wick Drive, Oak Lawn, IL 60453 (US). WENWORTH, Gary; 5540 North Wayne Avenue, Chicago, IL 60640 (US). SHAH, Urvil, B.; 9923 Cambridge Court, Mokena, IL 60448 (US). VU, Yen; 531 61st. Street, Apt. D, Westmont, IL 60559 (US).

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(54) Title: LOW POLARITY DIMERATE AND TRIMERATE ESTERS AS PLASTICIZERS FOR THERMOPLASTIC POLYMER/ELASTOMER COMPOSITES

(57) Abstract: A thermoplastic polymer/elastomer composite composition including one or more thermoplastic polymers, a natural or synthetic rubber, and a long chain cyclic dimerate ester and/or long chain cyclic trimerate ester plasticizer.

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**LOW POLARITY DIMERATE AND TRIMERATE ESTERS
AS PLASTICIZERS FOR THERMOPLASTIC
POLYMER/ELASTOMER COMPOSITES**

CROSS REFERENCE TO RELATED APPLICATION

5 This claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional
Patent Application Serial No. 60/396,453, filed July 17, 2002, the disclosure of which,
in its entirety, is incorporated herein by reference.

TECHNICAL FIELD

10 The present disclosure is directed to low polarity dimerate and/or
trimerate esters for plasticizing thermoplastic/elastomer composite compositions
including one or more thermoplastic polymers and one or more natural and/or
synthetic rubbers.

BACKGROUND

15 A number of thermoplastic polymers, elastomers, and their blends
(thermoplastic/elastomer composite compositions) are very difficult to plasticize. In
particular, thermoplastic/elastomer composite compositions that include one or more
thermoplastic polymers and one or more elastomers, such as EPDM, are difficult to
plasticize because it is difficult to find plasticizers that are sufficiently compatible
with the composite compositions. Consequently, exuding (bleeding) of plasticizer to
20 the surfaces of an article comprising the thermoplastic/elastomer composite
composition frequently occurs upon cooling and crystallization of the composite
composition.

25 Hydrocarbon-based processing oils such as naphthenic oils or
paraffinic oils are usually used to plasticize thermoplastic/elastomer composite
compositions containing elastomers such as EPDM. While hydrocarbon-based
processing oils can be used to plasticize such composite compositions with partial
success, the resulting plasticized compositions lack advantageous low temperature
properties. Moreover, the processing oils have a tendency to exude (bleed) to the
surfaces of articles manufactured from composite compositions. Attempts to use
30 conventional linear dibasic acid esters, such as dioctyl adipate or di-2-ethylhexyl

sebacate, or phthalate esters, such as di-2-ethylhexyl phthalate, have also been unsuccessful since such conventional ester plasticizers are either incompatible with composite compositions, resulting in exudation of the plasticizer, or are too volatile for many thermoplastic/elastomer composite composition uses.

5 U.S. Patent No. 5,290,886 teaches using organic ester plasticizers to plasticize thermoplastic elastomers comprising a blend of a thermoplastic polyolefin and an elastomer to lower the glass transition temperature (T_g) of both the elastomer and the polyolefin phases and to improve impact strength at low temperatures. The '886 patent neither discloses nor suggests using the cyclic dimerate and/or cyclic
10 trimerate esters disclosed herein, and states that "polymeric dibasic esters and aromatic esters were found to be significantly less effective" (column 3, lines 62-64).

Surprisingly and unexpectedly, particular dimerate and/or trimerate esters designed to have very low polarity act as efficient plasticizers for thermoplastic/elastomer composite compositions. The resulting plasticized
15 compositions have excellent low temperature properties and exhibit little or no tendency of the plasticizer to exude or bleed to a surface of the composite composition. Using the low polarity dimerate and/or trimerate esters as a plasticizer gives the thermoplastic/elastomer composite compositions an advantageous balance of flexibility, impact resistance, and strength.

20 SUMMARY OF THE DISCLOSURE

In brief, the use of long chain cyclic dimerate and/or trimerate ester plasticizers formed from di-, and/or tri-carboxylic acids, reacted with an alcohol containing a C_3 - C_{24} alkyl group, in a composite composition comprising a natural or synthetic vulcanizable rubber and one or more thermoplastic polymers, unexpectedly
25 improves the low temperature properties of the plasticized composite composition in applications such as, belts, e.g., conveyor belts, automotive drive train belts, and transmission belts, hoses, motor mounts, gaskets, and the like. Additionally, by adding one or more long chain cyclic dimerate and/or trimerate esters (di-, and/or tri-esters) in accordance with the disclosure to a thermoplastic/elastomer composite
30 composition, particularly dimerate esters formed by reacting the dimers and/or trimers of C_{18} fatty acids with C_3 - C_{24} alcohols, preferably, C_3 - C_{18} alcohols, more preferably,

C₆-C₁₈ alcohols, the low temperature characteristics of the composite composition are surprisingly improved. Preferably, the long chain cyclic dimerate and/or trimerate ester plasticizers are formed by reacting a C₃-C₁₈ alcohol with a mixture of mono-, di-, and tri-fatty acids, e.g., primarily C₁₈ carboxylic acids, and their dimers and trimers.

5 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

 The long chain cyclic dimerate and/or trimerate ester plasticizers described herein are added to a combination of one or more thermoplastic polymers and one or more natural or synthetic rubbers, preferably together with a vulcanizing agent for the rubber component. The cyclic dimerate and/or trimerate ester(s) can be
10 added to the thermoplastic polymer(s), or to the elastomer(s), or to the combination of thermoplastic polymer(s) and elastomer(s). Surprisingly, the long chain cyclic ester plasticizers disclosed herein significantly increase the low temperature properties of the resultant plasticized composite compositions and provide an excellent and
15 unexpected balance of flexibility, impact resistance, and strength to the composite compositions.

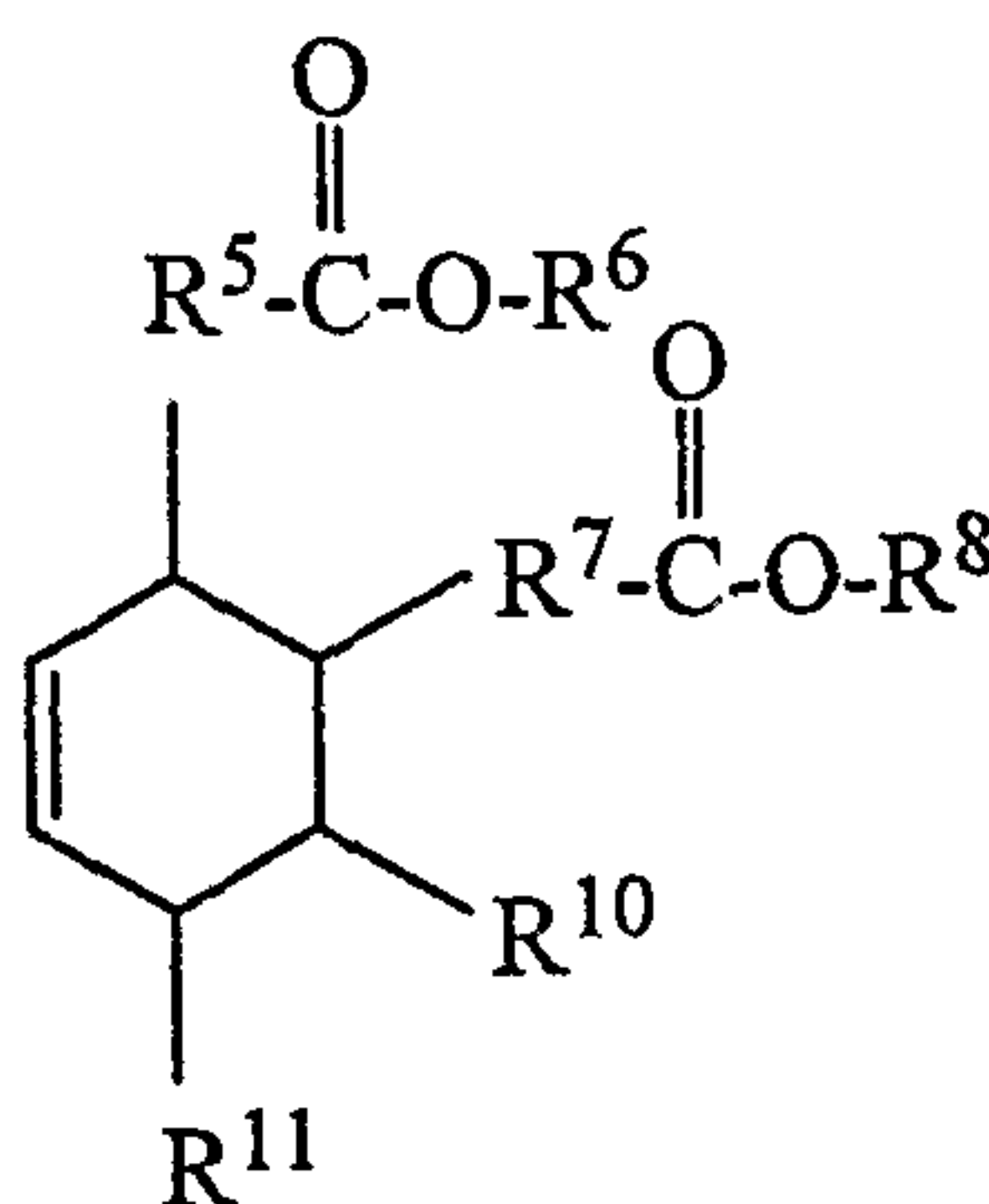
 The cyclic esters may be diesters, triesters, or mixtures thereof, that may include saturated or unsaturated hydrocarbon chains, straight chain or branched, having zero to six double bonds in the hydrocarbon chains. While cyclic monoesters are less preferred, they also may successfully be used in accordance with the present
20 disclosure.

 Many of the cyclic diester and/or cyclic triester materials are formed from self reaction of naturally derived fatty acid mixtures containing oleic, linoleic, and linolenic acids, and consequently are blends of mono-, di-, and tri-carboxylic acid esters. The ester blends may also include additional compounds that do not adversely
25 affect the advantages imparted to the thermoplastic polymer/elastomer composite composition by the subject cyclic dimerate and/or trimerate esters described herein.

 Ranges may be expressed herein as from "about" or "approximately" one particular value and/or to "about" or "approximately" another particular value. When such a range is expressed, another embodiment includes from the one particular
30 value and/or to the other particular value. Similarly, when values are expressed as

approximations, by use of the antecedent "about," it will be understood that the particular value forms another embodiment.

The cyclic diesters, referred to herein as dimerates, have a formula I, as follows:



(I)

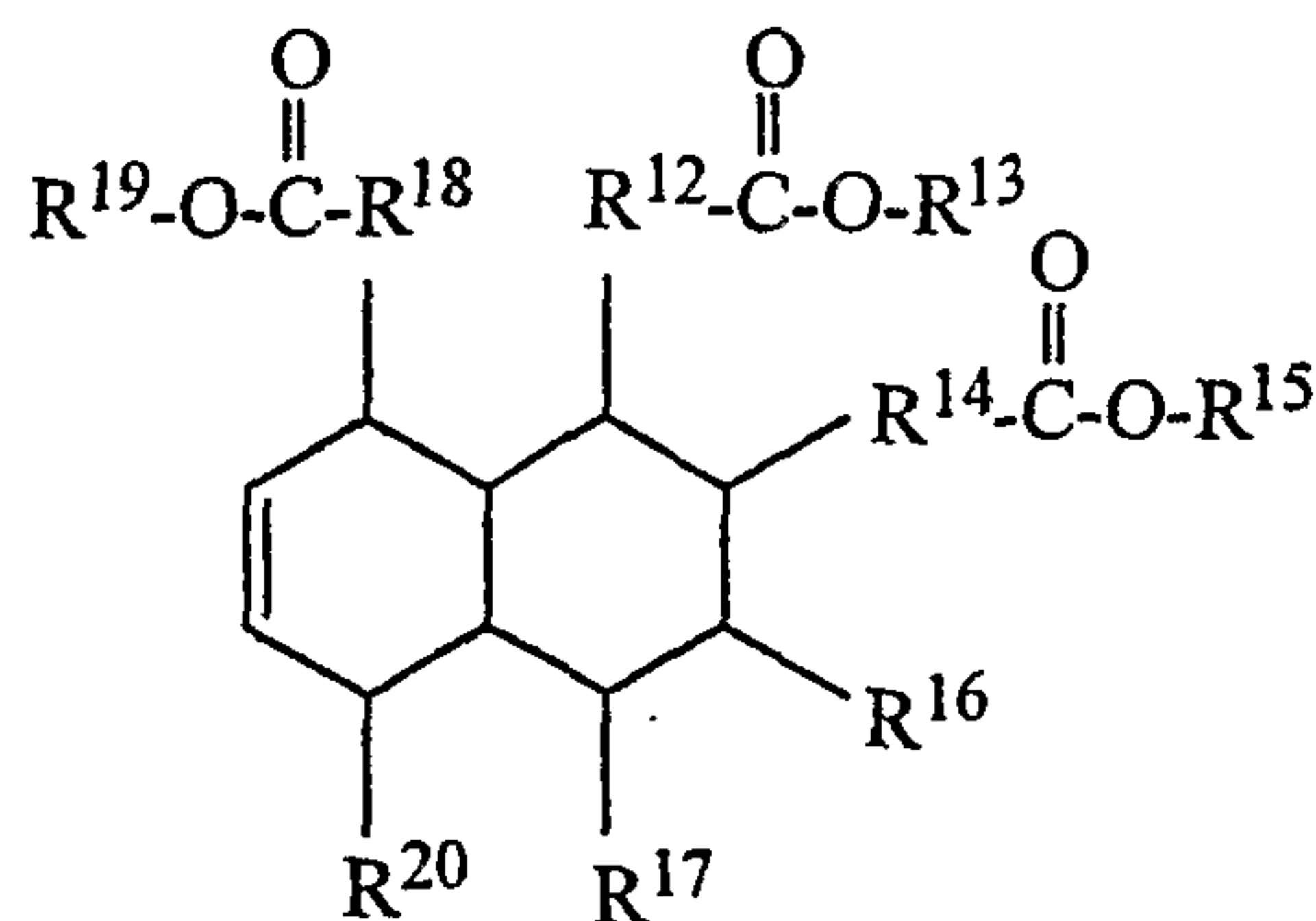
wherein R^5 and R^7 , same or different, are $\text{C}_3\text{-C}_{24}$, preferably $\text{C}_6\text{-C}_{24}$ hydrocarbon chains, more preferably $\text{C}_8\text{-C}_{18}$, straight chain or branched, either saturated or containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds;

R^6 and R^8 , same or different, are $\text{C}_3\text{-C}_{24}$ alkyl, preferably $\text{C}_3\text{-C}_{18}$ alkyl, more preferably $\text{C}_6\text{-C}_{18}$ alkyl, straight chain or branched, saturated, or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{10} and R^{11} , same or different, are a $\text{C}_3\text{-C}_{24}$, preferably $\text{C}_3\text{-C}_{18}$, more preferably $\text{C}_6\text{-C}_{18}$ saturated hydrocarbon chain, straight chain or branched; or an unsaturated $\text{C}_3\text{-C}_{24}$, preferably $\text{C}_3\text{-C}_{18}$, more preferably $\text{C}_6\text{-C}_{18}$ hydrocarbon chain, straight chain or branched, containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds.

The cyclic tri-esters, referred to herein as trimerates, have a formula II,

as follows:



(II)

wherein R^{12} , R^{14} and R^{18} , same or different, are a C_3 - C_{24} , preferably C_6 - C_{24} , more preferably C_8 - C_{18} hydrocarbon chain, straight chain or branched, either saturated or
 5 containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds;

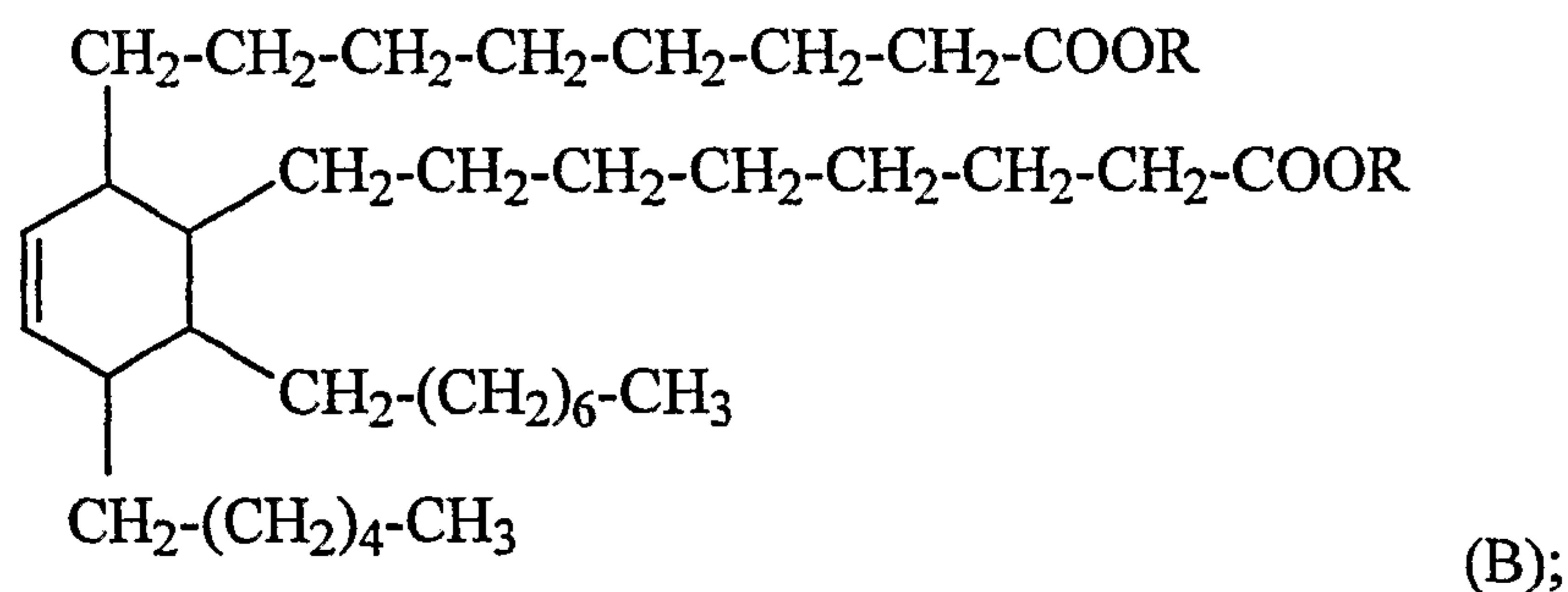
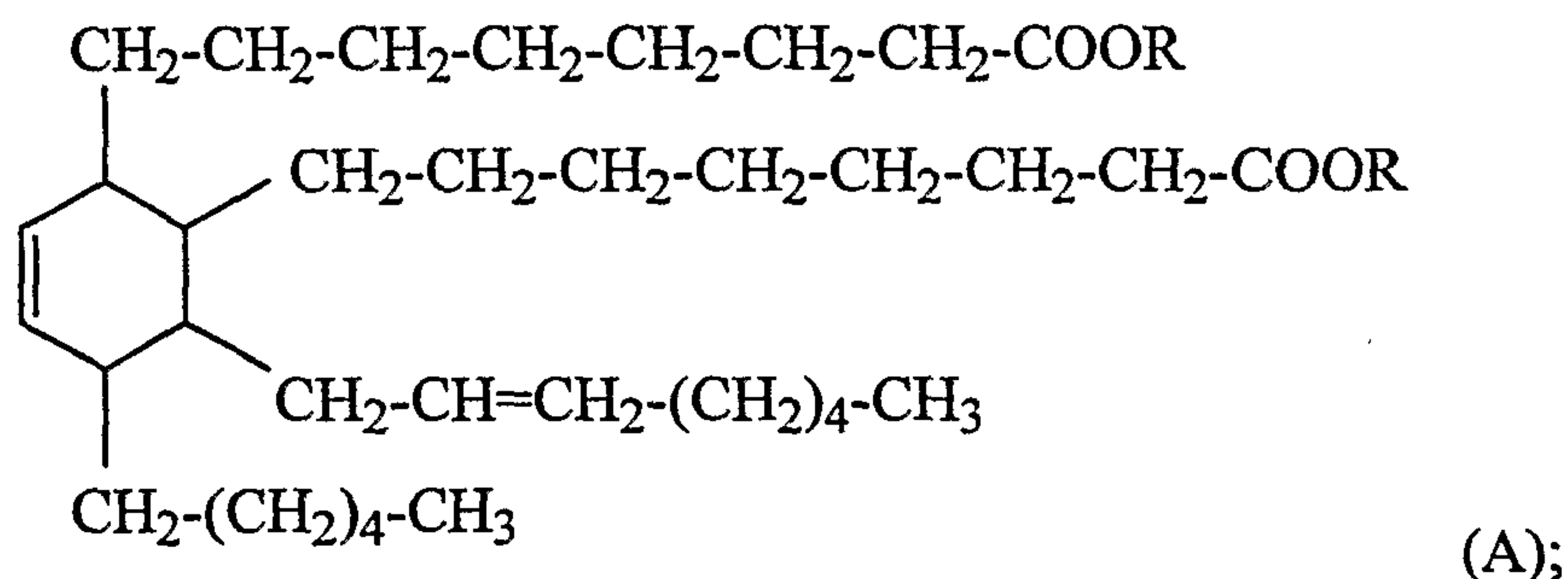
R^{13} , R^{15} and R^{19} , same or different, are C_3 - C_{24} alkyl, preferably C_3 - C_{18} hydrocarbon chains, more preferably C_6 - C_{18} alkyl, straight chain or branched, saturated, or
 10 unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are C_3 - C_{24} , preferably C_3 - C_{18} saturated hydrocarbon chains, more preferably C_6 - C_{18} , straight chain or branched; or
 15 unsaturated C_3 - C_{24} , preferably C_3 - C_{18} , hydrocarbon chains, more preferably C_6 - C_{18} , straight chain or branched, containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds.

The low polarity of the cyclic ester compounds disclosed herein is important for successfully plasticizing thermoplastic/elastomeric composite compositions. Low polarity cyclic ester compounds, e.g., ester compounds formed from dimer acids having only acidic carboxyl groups (i.e., the dimer acids do not
 20 contain other non-acidic hydroxyl substituents) and alcohols having a single hydroxyl group are preferred. Similarly, it is preferred that R^6 , R^8 , R^{13} , R^{15} and R^{19} of formulas I and II do not contain hydroxyl substituents. Dimerate esters formed from dimer acids and glycol type alcohols, for example, glycol alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, and other polyethylene glycols, would be
 25 too polar to plasticize thermoplastic/elastomeric composite compositions while simultaneously providing superior low temperature properties. Additionally, esters

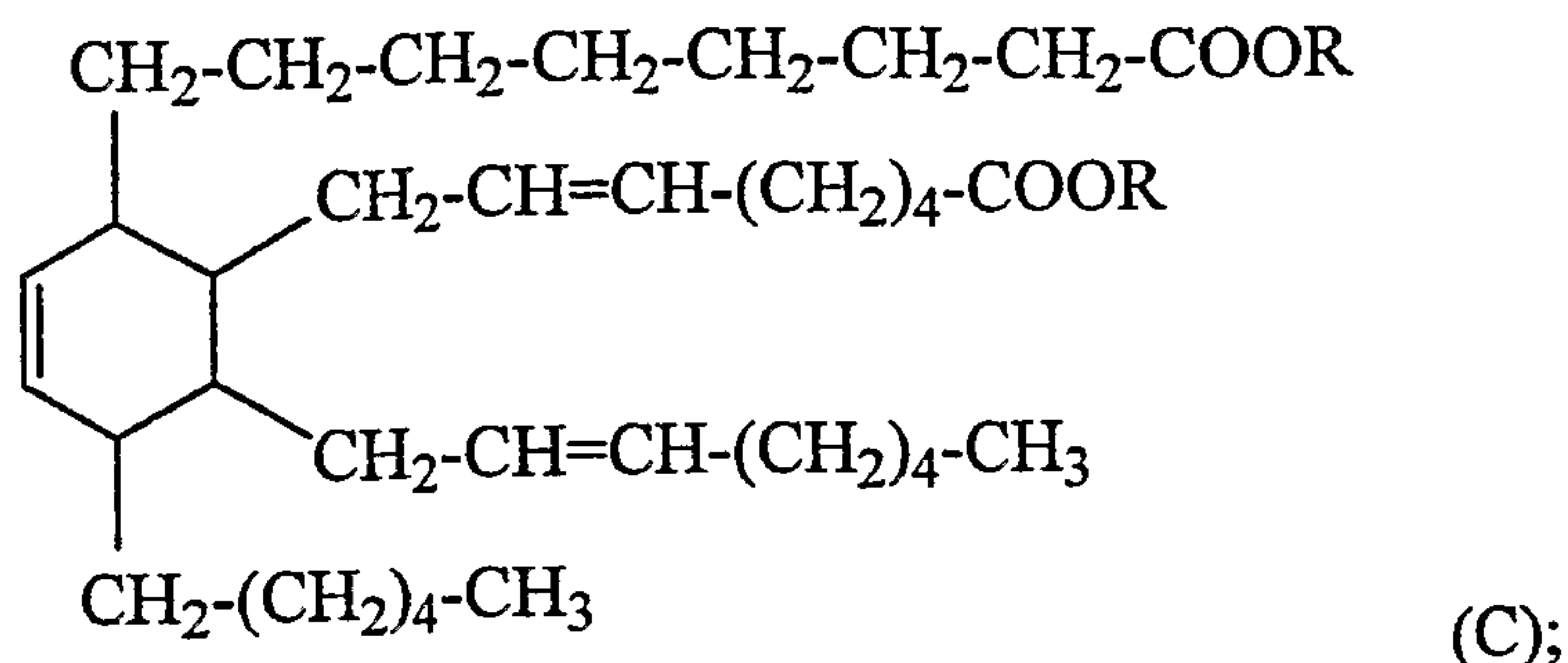
prepared by reacting dimer acids with the glycol functionalized monomers and oligomers set forth in U.S Pat. No. 4,054,561 would also be too polar for use as plasticizers for composite compositions.

Useful cyclic diesters falling within formula I include dimerate ester
 5 structures formed by the reaction of a C₃₆ dimer acid derived from tall oil fatty acids and C₃-C₂₄, preferably C₃-C₁₈, more preferably C₆-C₁₈ alcohol, straight chain or branched, saturated, or unsaturated containing 1 to 3 carbon-to-carbon double bonds. Examples of such cyclic esters include the following structures, wherein the dimer
 10 acid corresponding to structure A is formed by self reaction of linoleic acid, the dimer acid corresponding to structure B is formed by reacting linoleic acid with oleic acid, and the dimer acid corresponding to structure C is formed by reacting linoleic acid with linolenic acid:



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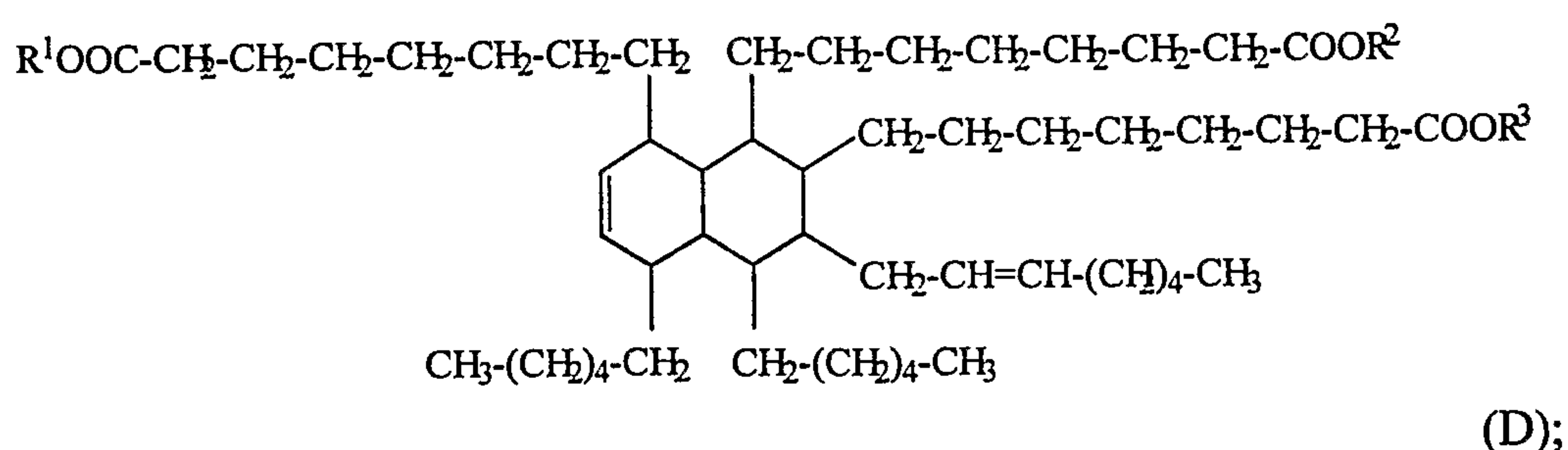
and



wherein each R, same or different, in formulas (A), (B), and (C) is a C₃-C₂₄ radical, preferably C₃-C₁₈, more preferably C₆-C₁₈, straight chain or branched, saturated, or unsaturated containing 1 to 3 carbon-to-carbon double bonds.

RX-13804, RX-13824, and RX-13892 are additional examples of dimerate esters in accordance with formula I. RX-13804 is formed by the reaction of a predominantly C₃₆ dimer acid with 2-ethylhexyl alcohol. RX-13824 is formed by the reaction of a predominantly C₃₆ dimer acid with tridecyl alcohol. RX-13892 is formed by the reaction of a predominantly C₃₆ dimer acid with oleyl alcohol.

A representative example of a triester (trimerate ester) in accordance with formula II is the following structure (D):



wherein each R¹, R², and R³, same or different, is a C₃-C₂₄ radical, preferably C₃-C₁₈, more preferably C₆-C₁₈, straight chain, or branched, saturated, or unsaturated containing 1 to 3 carbon-to-carbon double bonds.

In the description, the term dimerate is sometimes used when referring to blends including components having structures in accordance with both formulas I and II (i.e., dimerates and trimerates).

The cyclic ester plasticizers of formulas I, II, or mixtures thereof are typically added to a composite composition in an amount of about 0.1 parts to about 45 parts by weight, preferably from about 5 parts to about 40 parts, more preferably from about 10 parts to about 35 parts per 100 parts by weight of the thermoplastic/elastomer composite composition.

A particularly useful blend of carboxylic acids for forming cyclic esters in accordance with the invention is a blend of carboxylic acids known as dimer acid, CAS#: 61788-89-4, which is a blend including, primarily, C₃₆ and C₅₄ dimer and trimer acids, and predominantly (more than 50% by weight) C₃₆ dimer acid.

The fatty acid residues or hydrocarbon chains R⁵, R⁷, R¹², R¹⁴ and R¹⁸ of the esters of formulas I and II can be any C₃-C₂₄, preferably, C₆-C₂₄, more preferably C₈-C₁₈, hydrocarbon chain, either saturated or containing 1 to 6, preferably 1 to 3, carbon-to-carbon double bonds, derived from animal or vegetable fatty acids such as butter; lard; tallow; grease; herring; menhaden; pilchard; sardine; babassu; castor; coconut; corn; cottonseed; jojoba; linseed; oiticica; olive; palm; palm kernel; peanut; rapeseed; safflower; soya; sunflower; tall; and/or tung. Examples are the hydrocarbon chain residues from the following fatty acids, where the number in parentheses indicates the number of carbon atoms, and the number of double bonds, e.g., (C₂₄₋₆) indicates a hydrocarbon chain having 24 carbon atoms and 6 double bonds: hexanoic (C₆₋₀); octanoic (C₈₋₀); decanoic (C₁₀₋₀); dodecanoic (C₁₂₋₀); 9-dodecenoic (CIS) (C₁₂₋₁); tetradecanoic (C₁₄₋₀); 9-tetradecenoic (CIS) (C₁₄₋₁); hexadecanoic (CIS) (C₁₆₋₀); 9-hexadecenoic (CIS) (C₁₆₋₁); octadecanoic (C₁₈₋₀); 9-octadecenoic (CIS) (C₁₈₋₁); 9,12-octadecadienoic (CIS, CIS) (C₁₈₋₂); 9, 12, 15-octadecatrienoic (CIS, CIS, CIS) (C₁₈₋₃); 9, 11, 13-octadecatrienoic (CIS, TRANS, TRANS) (C₁₈₋₃); octadecatetraenoic (C₁₈₋₄); eicosanoic (C₂₀); 11-eicosenoic (CIS) (C₂₀₋₁); eicosadienoic (C₂₀₋₂); eicosatrienoic (C₂₀₋₃); 5, 8, 11, 14-eicosatetraenoic (C₂₀₋₄); eicosapentaenoic (C₂₀₋₅); docosanoic (C₂₂); 13-docosenoic (CIS) (C₂₂₋₁); docosatetraenoic (C₂₂₋₄); 4, 8, 12, 15, 19-docosapentaenoic (C₂₂₋₅); docosahexaenoic (C₂₂₋₆); tetracosenoic (C₂₄₋₁); and 4, 8, 12, 15, 18, 21-tetracosahexaenoic (C₂₄₋₆).

Commercially available blends of useful polybasic acids that can be reacted with C₃-C₂₄, preferably C₃-C₁₈, more preferably C₆-C₁₈ alcohols, straight

chain or branched, saturated, or unsaturated containing 1 to 3 carbon-to-carbon double bonds to produce the dimerate and trimerate esters, as blends, include the following: EMPOL® 1010 Dimer Acid; EMPOL® 1014 Dimer Acid; EMPOL® 1016 Dimer Acid; EMPOL® 1018 Dimer Acid; EMPOL® 1022 Dimer Acid; EMPOL® 1024
5 Dimer Acid; EMPOL® 1040 Trimer Acid; EMPOL® 1041 Trimer Acid; EMPOL® 1052 Polybasic Acid; and similar PRIPOL™ products from Uniqema as well as UNIDYME® products from Arizona Chemical.

Particularly useful long chain ester additives are made by reacting any of the long chain mono, dimer and/or trimer acids with one or more straight chain or
10 branched C₃-C₂₄, preferably C₃-C₁₈, more preferably C₆-C₁₈ alcohols to produce the esters of formulas I and II. The above dimer, trimer, and polybasic acids are produced by dimerizing, trimerizing, and polymerizing (oligomerizing) long chain carboxylic acids from fatty acids. The fatty acids are typically mixtures. For example, the dimer acid produced from a C₁₈ carboxylic acid (e.g., a mixture of stearic, oleic, linoleic, and
15 linolenic) will typically result in a blend of numerous cyclic dimerate and trimerate esters, as in formulas I and II, some saturated and some containing hydrocarbon chains having 1 to 6, generally 1 to 3, carbon-to-carbon double bonds. Any one, or any blend, of the esters that includes the cyclic dimerate and/or cyclic trimerate esters of formulas I or II will function to plasticize thermoplastic polymer/elastomer
20 composite materials, and provide a balance of flexibility, strength, and low temperature properties with essentially no bleeding of the plasticizer to the surface of the composite composition. Particularly, the composite compositions described herein are characterized in that the low temperature properties are improved to provide the composite compositions a balance of good flexibility and strength at low
25 temperatures.

The dimerate and trimerate esters of the disclosure may be used to plasticize thermoplastic polymer/elastomer composite compositions. The terms thermoplastic alloys and thermoplastic vulcanizates also describe composite compositions in accordance with the disclosure.

30 As used herein, thermoplastic polymers generally include synthetic high polymers that soften when exposed to heat and return to their original state when

cooled to room temperature. More specifically, thermoplastic polymers useful in the composite compositions described herein include polyvinyl chlorides, nylons, propylene/ α -olefin copolymers, polyethylenes, ethylene/ α -olefin copolymers, polyurethane prepolymers, polystyrenes such as styrene/ethylene and hydrogenated
5 styrene/butadiene block copolymers, polypropylenes, cellulosic resins, and acrylic resins. Preferably, the plasticizers described herein plasticize composite compositions including thermoplastics such as polypropylenes, propylene/ α -olefin copolymers, and ethylene/ α -olefin copolymers.

Rubbers useful in the composite compositions described herein can be
10 natural rubbers (NR) and/or synthetic rubbers. Synthetic rubbers include homopolymers of conjugated diene compounds, such as isoprene, butadiene, chloroprene and the like, for example, polyisoprene rubber (IR), polybutadiene rubber (BR), polychloroprene rubber and the like; copolymers of the above described conjugated diene compounds with vinyl compounds, such as styrene, acrylonitrile,
15 vinyl pyridine, acrylic acid, methacrylic acid, alkyl acrylates, alkyl methacrylates and the like, for example, styrene-butadiene copolymeric rubber (SBR), vinylpyridine-butadiene-styrene copolymeric rubber, acrylonitrile-butadiene copolymeric rubber, acrylic acid-butadiene copolymeric rubber, methacrylic acid-butadiene copolymeric rubber, methyl acrylate-butadiene copolymeric rubber, methyl methacrylate-butadiene
20 copolymeric rubber, acrylonitrile-butadiene-styrene terpolymer, and the like; copolymers of olefins, such as ethylene, propylene, isobutylene and the like with dienes, for example isobutylene-isoprene copolymeric rubber (IIR); copolymers of olefins with non-conjugated dienes, for example, ethylene-propylene-diene rubbers (EPDM) such as ethylene-propylene-cyclopentadiene terpolymer, ethylene-propylene-
25 5-ethylidene-2-norbornene terpolymer and ethylene-propylene-1,4-hexadiene terpolymer; polyalkenamer obtained by ring opening polymerization of cycloolefins, for example, polypentenamer; rubbers obtained by ring opening polymerization of oxirane ring, for example, polyepichlorohydrin rubber and polypropylene oxide rubber which can be vulcanized with sulfur, and the like. Furthermore, halides of the
30 above-described various rubbers, for example, chlorinated isobutylene-isoprene copolymeric rubber (CI-IIR), brominated isobutylene-isoprene copolymeric rubber (Br-IIR), fluorinated polyethylene, and the like are included.

Of course, the plasticizers in accordance with the present disclosure can be applied to composite compositions comprising other rubbers. Additionally, all of these rubbers may be kneaded with compounding agents conventionally used for compounding with rubber, for example, fillers, such as carbon black, silica, calcium carbonate, lignin and the like, softening agents, such as mineral oils, vegetable oils,
5 prior to vulcanization.

In order to cure a rubber containing composite composition, a vulcanizing agent such as a sulfur or peroxide vulcanizing agent is dispersed throughout the composition. The amount of vulcanizing agent, e.g., sulfur, in the
10 composition is typically from about 2 to about 8 parts, for example from about 3 to about 6, by weight per 100 parts by weight of natural and/or synthetic rubber, but lesser or larger amounts, for example from about 1 to about 10 parts on the same basis, may be employed. A preferred range is from about 2.5 to about 6 parts per 100 parts by weight of rubber. Representative examples of sulfur vulcanizing agents
15 include elemental sulfur (S_8), amine disulfides, polymeric polysulfides, and sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur.

The term "vulcanization" used herein means the introduction of three dimensional cross-linked structures between rubber molecules. Thus, thiuram vulcanization, peroxide vulcanization, quinoid vulcanization, resin vulcanization,
20 metal salt vulcanization, metal oxide vulcanization, polyamine vulcanization, radiation vulcanization, hexamethylenetetramine vulcanization, urethane cross-linker vulcanization, and the like are included in addition to sulfur vulcanization which is usual and most important.

Accelerators may be used to control the time and/or temperature
25 required for vulcanization and to improve the properties of the vulcanizate. The accelerator(s) may be used in total amounts ranging from about 0.3 parts to about 4 parts, for example about 0.3 parts to about 1.5 parts, preferably from about 0.4 parts to about 1.0 parts and more preferably from about 0.5 parts to about 0.8 parts by weight per 100 parts by weight of natural and/or synthetic rubbers. Suitable types of
30 accelerators that may be used are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. If included in the rubber

containing composite composition, the primary accelerator preferably is typically a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound. Specific examples of vulcanization accelerators which can be used in the rubber containing composite compositions described herein are thiazole-based accelerators, for example 2-mercaptobenzothiazole, bis(2-benzo-thiazolyl)disulphide, 2(2',4'-dinitro-phenylthio)benzothiazole, benzothiazole-2-sulphenamides for instance N-isopropyl-benzothiazole-2-sulphenamide, N-tert-butyl-benzothiazole-2-sulphenamide, N-cyclohexylbenzo-thiazole-2-sulphen-amide, and 2(morpholinothio)benzothiazole, and thiocarbamylsulphenamides, for example N,N-dimethyl-N',N'-dicyclohexylthiocarbamoylsulphenamide and N(morpholinothiocarbonylthio)morpholine.

The commonly employed carbon blacks used in conventional rubber compounding applications can be used as the carbon black in the plasticizers in accordance with this disclosure. Representative examples of such carbon blacks include N110, N121, N220, N231, N234, N242, N293, N299, S315, N326, N330, M332, N339, N343, N347, N351, N358 and N375.

The rubber containing composite compositions described herein are compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable or peroxide-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, sulfur donors, curing aids, such as activators and retarders and processing additives, such as oils, resins including tackifying resins and other conventional plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, retarders and peptizing agents.

Typical amounts of zinc oxide comprise about 2 parts to about 5 parts per 100 parts by weight of total polymer. Typical amounts of waxes comprise about 1 part to about 5 parts per 100 parts by weight of total polymer. Often microcrystalline waxes are used. Typical amounts of retarders range from about 0.05 parts to about 2 parts per 100 parts by weight of total polymer. Typical amounts of peptizers comprise about 0.1 parts to about 1 part per 100 parts by weight of total polymer.

Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide.

Vulcanization of the rubber containing composite compositions described herein is generally carried out at conventional temperatures ranging from
5 about 100°C. to about 200°C. Preferably, the vulcanization is conducted at temperatures ranging from about 110°C. to about 180°C. Any of the usual vulcanization processes may be used such as heating in a press or mold, heating with superheated steam or hot air or in a salt bath.

Upon vulcanization of the rubber containing composite composition at
10 a temperature ranging from about 100°C. to about 200°C., the rubber containing composite composition can be used for various purposes. For example, the vulcanized rubber containing composite composition may be in the form of belts, hoses, gaskets and air springs.

The plasticizers in accordance with the present disclosure may be
15 better understood by reference to the following examples in which parts and percentages are by weight unless otherwise indicated.

Procedure

The following general procedure was used in the preparation of
20 thermoplastic/elastomer composite compositions disclosed in the following tables. The thermoplastic polymer(s) and rubber component(s) were placed in a heated internal mixer, with an appropriate portion of a cyclic ester plasticizer in accordance with the disclosure (and other desired additives). Typically, approximately one third of the total plasticizer amount was added at this time to aid in mixing. The mixture
25 was heated to a temperature sufficient to melt the polyolefin component and was then masticated. After a maximum of mixing torque indicated that vulcanization had occurred, the remaining portion of the plasticizer was added, and mixing was continued until the desired degree of vulcanization was achieved. The order of addition of the various components may vary.

30 More specifically, the rubber compound(s), the thermoplastic polymer(s), a phenolic curing agent and additives were blended in an electrically

heated Haake mixer at a mixing speed of about 77 rpm and at a temperature ranging between about 120 °C to about 190 °C. Before melting of the polyolefin component, a Lewis acid was added, and mixing was continued. The mixing temperature as a function of time was observed, and the onset of vulcanization of the rubber portion
5 was accompanied by a rapid increase in mixing torque at around 180 °C. The crosslinking of the rubber component causes the increase in viscosity of the mixture and the need for additional energy to mix the thermoplastic vulcanizate. Mixing was stopped when the torque measurement was relatively constant over time. The compositions were removed from the mixer and sheets were molded at about 190 °C
10 and used for measurement of physical properties.

Results

Table I compares the effectiveness of dimerate plasticizers in accordance with the disclosure with a conventional linear dibasic acid ester, dioctyl sebacate. The dimerate esters plasticized a thermoplastic/elastomer blend comprising
15 polypropylene and EPDM about as well as, and in some cases better than, the conventional plasticizer DOS. For example, the fusion viscosity values for the composites plasticized with RX 13824 and RX 13804 demonstrate the efficacy of the disclosed plasticizers.

Table I

Example	1	2	3	4
PDC 1280	50.0			
Royalene IM7200	50.0			
Kadox 930	2.0			
Stearic Acid	0.5			
DOS	15	---	---	---
RX 13824	---	15	---	---
RX 13804	---	---	15	---
TDT	---	---	---	15
TOTAL	117.5			
<u>Mill Addition</u>				
Trigonox	0.5			
TOTAL	118.0			
Major Variable	DOS	RX 13824	RX 13804	TDT
<u>Original Physical Properties</u>				
Stress @ 100% Elong. MPa	8.8	8.5	8.9	8.0
psi	1276.4	1232.8	1290.9	1160.3
Stress @ 200% Elong. MPa	9.4	8.8	9.4	8.5
Stress @ 300% Elong. MPa	10.0	n/a	8.1	9.0
Tensile Strength, MPa	12.2	10.4	10.8	11.7
psi	1772	1510	1561	1700
Elongation @ Break, %	538	358	404	555
Toughness, Psi	7619	4643	5455	7293
Harness Duro A, pts.				
Specific Gravity	0.914	0.912	0.914	0.910
Clear Point, °F, DOP-1201-010				
Fusion Viscosity, 77 RPM, 180 EC				
Fusion Torque, mg	1900	1400	1600	1800
Fusion Temperature, EC	193	190	190	193
Melt Torque, mg	715	733	739	683
Energy kJ	50	42	45	45

Table II compares the effectiveness of dimerate plasticizers in accordance with the disclosure with a conventional linear dibasic acid ester, dioctyl sebacate and with a conventional hydrocarbon-based processing oil, paraffinic oil. The dimerate esters plasticized a composite thermoplastic/elastomer blend comprising polypropylene and EPDM about as well as, and in some cases better than, the conventional plasticizers DOS and paraffinic oil. For example, the stress and fusion viscosity values for the composites plasticized with RX 13824 and RX 13804 demonstrate the efficacy of the disclosed plasticizers. An example illustrating the physical properties of an unplasticized composite composition is also included in Table II for comparison purposes.

Table II

Example	5	6	7	8	9	10
PDC 1280	50.00					
Royalene IM7200	50.00					
Kadox 930	2.0					
Stearic Acid	1.0					
DOS	---	20.00	---	---	---	---
RX 13824	---	---	20.00	---	---	---
RX 13804	---	---	---	20.00	---	---
TDT	---	---	---	---	20.00	---
Sunpar 2280	---	---	---	---	---	20.00
Subtotal	103.00	123.00				
Mill Addition						
SP-1056	5.00					
TOTAL	108.00	128.00				
Major Variable	Uplasticized	DOS	RX 13824	RX 13804	TDT	Process Oil
Original Physical Properties						
Stress @ 100% Elong. MPa	16.4	9.4	8.8	8.7	8.3	10.2
psi	2379	1363	1276	1262	1204	1479
Stress @ 200% Elong. MPa	na	12.0	10.9	10.8	10.3	12.4
Stress @ 300% Elong. MPa	na	15.2	13.4	13.1	12.6	14.9
Tensile Strength, MPa	21.1	20.6	19.2	18.4	18.9	18.2
psi	3059	2987	2780.0	2664.0	2738.0	2635.0
Elongation @ Break, %	262	407	445.0	451.0	468.0	387.0
Toughness, Psi	6478	7324	7598.0	7586.0	7731.0	6926.0
Hardness Duro D, pts.	52	35	37	36	35	39
<u>Fusion Viscosity, 77 RPM, 180 EC**</u>						
Fusion Torque, mg	2400	1900	1900	1900	1900	1900
Fusion Temperature, EC	195	194	194	191	190	192
Melt Torque, mg	1040	604	600	617	525	668
Energy, kJ	67.4	45.6	43.3	45.1	41.6	46.3

**Plasticizer added after fusion peak

Table III provides glass transition temperature data for several plasticized composite compositions, and demonstrates that plasticizers in accordance with the disclosure plasticize composite compositions better than conventional plasticizing compositions such as paraffinic oils. The glass transition temperature for both the rubber and plastic components illustrates the efficacy of a plasticizer in accordance with the invention in improving the low temperature behavior of a thermoplastic/elastomer composite composition. Table III also contains data (see example 12 weight change, % after heat aging) illustrating the volatility of conventional dibasic linear esters such as DOS. The heat aging data demonstrates that the dimerate esters RX-13804 and RX-13824 have a marked improvement over conventional dibasic linear esters such as DOS and monoester compounds such as tridecyl tallate (TDT) because significantly lower weight losses and hardness changes are observed in the dimerate ester formulations.

Table III

Example	11	12	13	14	15	16	17
PDC 1280	50.00						
Royalene IM7200	50.00						
Kadox 930	1.00						
Stearic Acid	1.00						
SnCl ₂ ·2H ₂ O	0.50						
DOS	--	30.00	--	--	--	--	--
RX-13824	--	--	30.00	--	--	--	--
RX-13804	--	--	--	30.00	--	--	--
TDT	--	--	--	--	30.00	--	--
Sunpar 150	--	--	--	--	--	30.00	--
RX-13892	--	--	--	--	--	--	30.00
SP-1045	5.00						
Total	107.50	137.50	137.50	137.50	137.50	137.50	137.50
Major Variable	Un-plasticized	DOS	RX-13824	RX-13804	TDT	Sunpar 150	RX-13892
Original Physical Properties							
Stress @ 100% Elong., MPa	14.7	8.2	7.9	8.6	7.4	8.1	7.6
Stress @ 200% Elong., MPa	2132	1189	1146	1247	1073	1175	1102
Stress @ 300% Elong., MPa	17.2	10.9	10.6	11.4	9.6	10.6	9.9
Tensile Strength, MPa	14.4	13.8	14.8	12.1	13.8	12.6	
psi	28.0	19.3	21.9	20.5	19.7	22.1	18.9
Elongation @ Break, %	4065	2803	3175	2971	2855	3200	2735
Toughness, psi	384	390	443	399	469	443	436
Hardness Duro A, pts.	10037	6285	7575	6787	7384	7626	6784
Specific Gravity	50	31	30	31	30	33	31
Air Oven Aging, 2 wks. @ 125°C							
Stress @ 100% Elong., MPa	14.6	11.4	7.5	8.0	8.8	8.2	7.6
Stress Change, %	2118	1654	1088	1160	1276	1189	1102
Tensile Ultimate @ Break, MPa	-1	39	-5	-7	19	1	0
psi	25.5	25.8	19.5	19.1	26.5	22.6	18.2
Tensile Change, %	3693	3747	2825	2767	3847	3271	2645
Elongation @ Break, %	-9	34	-11	-7	35	2	-3
Elongation Change, %	346	401	434.5	397	511	417	422
Toughness, psi	-10	3	-2	-1	9	-6	-3
Toughness Change, %	8641	8768	6941	6428	10108	7415	6579
Hardness Duro A, pts	-14	40	-8	-5	37	-3	-3
Hardness Change, pts	50	50	34	34	39	35	35
Weight Change, %	0	19	4	3	9	2	4
Glass Transition Temperature							
Rubber T _g (°C)	-0.3	-21.6	-1.5	-1.3	-12.5	-0.8	-1.7
Plastic T _g (°C)	-22	-37	-38	-38	-47	-29	--
	8	-16	-17	-17	-22	2	--

Table IV provides additional example formulations comparing the effectiveness of dimerate plasticizers with the conventional linear dibasic acid ester, dioctyl sebacate, and a conventional plasticizing processing oil. The dimerate esters plasticized a thermoplastic/elastomer blend comprising polypropylene and EPDM about as well as, and in some cases better than, the conventional plasticizer DOS. Additionally, the air oven aging data indicates that the conventional linear dibasic acid ester DOS is relatively volatile (e.g., greater weight loss) when compared with the dimerate ester plasticizers in accordance with the disclosure.

Table IV

Example	18	19	20	21	22	23	24
PDC 1280	50.00						
Royalene IM7200	50.00						
Kadox 930	1.00						
Stearic Acid	1.00						
SnCl ₂ ·2H ₂ O	1.00						
DOS	--	20.00	--	--	--	--	--
RX-13824	--	--	20.00	--	--	--	--
RX-13804	--	--	--	20.00	--	--	--
TDT	--	--	--	--	20.00	--	--
Sunpar 150	--	--	--	--	--	20.00	--
RX-13892	--	--	--	--	--	--	20.00
Subtotal	103.00	123.00	123.00	123.00	123.00	123.00	123.00
<u>Mill Addition</u>							
SP-1045	5.00						
Total	108.00	128.00	128.00	128.00	128.00	128.00	128.00
Major Variable	Un-						
	plasticized	DOS	RX-13824	RX-13804	TDT	Process Oil	RX-13892
<u>Original Physical Properties</u>							
Stress @ 100% Elong., MPa	14.7	9.2	9.1	9.0	8.9	9.8	8.5
psi	2132	1334	1320	1305	1291	1421	1233
Stress @ 200% Elong., MPa	17.2	12.1	11.7	11.6	11.6	12.5	10.8
Stress @ 300% Elong., MPa	--	15.7	14.9	14.8	14.7	15.8	13.6
Tensile Strength, MPa	28.0	22.1	24.2	23.7	21.3	20.4	20.7
psi	4065	3200	3517	3438	3083	2965	3002
Elongation @ Break, %	384	400	443	439	416	381	442
Toughness, psi	10037	7268	8472	8231	7361	6928	7575
Hardness Duro A, pts.	50	35	36	36	35	40	35
Specific Gravity	0.910	0.910	0.911	0.914	0.909	0.910	0.912
<u>Melt Viscosity 77 RPM, 180 °C</u>							
Fusion Torque, mg	2844	1396	1121	1162	1233	1386	--
Fusion Temperature, C	168	160.7	170	168.7	160.7	167.6	--
Melt Torque, mg	1106	593	634	620	528	670	--
Energy, kJ	67.7	40.3	34.4	37.3	37.1	42.5	--
<u>Air Oven Aging, 2 wks. @ 125°C</u>							
Stress @ 100% Elong., MPa	14.6	11.5	9.2	9.2	10.3	9.8	8.7
psi	2118	1668	1334	1334	1494	1421	1262
Stress Change, %	-1	25	1	2	16	0	2
Tensile Ultimate @ Break, MPa	25.5	25.1	24.2	22.3	23.0	22.1	19.6
psi	3693	3642	3504	3234	3341	3212	2849
Tensile Change, %	-9	14	0	-6	8	8	-5
Elongation @ Break, %	346	385.6	433	394	411	360	402
Elongation Change, %	-10	-4	-2	-10	-1	-6	-9
Toughness, psi	8641	8393	8434	7359	8233	6848	6882
Toughness Change, %	-14	15	0	-11	12	-1	-9
Hardness Duro A, pts	50	50	39	39	44	40	37
Hardness Change, pts	0	15	3	3	9	0	2
Weight Change, %	-0.3	-15.8	-1.4	-1.3	-10.0	-0.8	-1.5

Table V provides additional formulations incorporating plasticizers in accordance with the disclosure and compares the effectiveness of dimerate plasticizers with the conventional linear dibasic acid ester, dioctyl sebacate, and a conventional plasticizing processing oil.

Table V

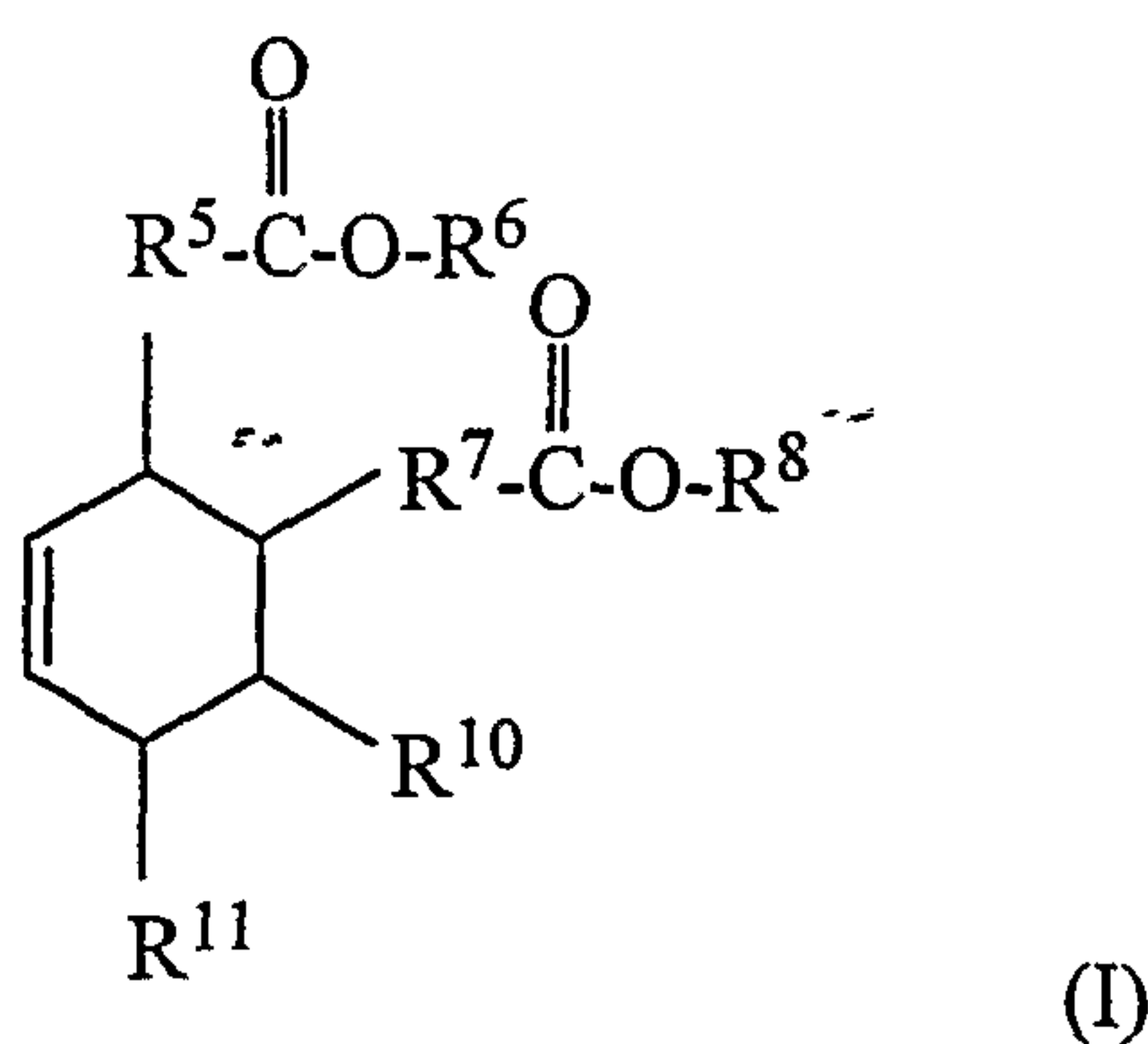
Example	25	26	27	28	29	30	31
PDC 1280	50.00						
Royalene IM7200	50.00						
Kadox 930	1.00						
Stearic Acid	1.00						
SnCl ₂ ·2H ₂ O	0.50						
DOS	--	10.00	--	--	--	--	--
RX-13824	--	--	10.00	--	--	--	--
RX-13804	--	--	--	10.00	--	--	--
TDT	--	--	--	--	10.00	--	--
Sunpar 150	--	--	--	--	--	10.00	--
RX13892	--	--	--	--	--	--	10.00
Subtotal	102.50	112.50	112.50	112.50	112.50	112.50	112.50
Mill Addition							
SP-1045	5.00						
Total	107.50	117.50	117.50	117.50	117.50	117.50	117.50
Major Variable	Un-plasticized	DOS	RX-13824	RX-13804	TDT	Process Oil	RX-13892
Original Physical Properties							
Stress @ 100% Elong., MPa		11.0	11.2	10.9	10.1	11.0	10.8
psi		1595	1624	1581	1465	1595	1566
Stress @ 200% Elong., MPa		14.0	14.1	13.5	12.4	13.8	13.6
Stress @ 300% Elong., MPa		18.4	18.2	17	15.5	17.6	17.3
Tensile Strength, MPa		27.2	24.4	21.5	23.1	27.8	25.9
psi		3940	3543	3116	3349	4025	3753
Elongation @ Break, %		409	386	376	429	432	422
Toughness, psi		8945	8121	7387	8376	9627	9030
Hardness Duro A, pts.		39	42	42	40	45	41
Specific Gravity		0.909	0.910	0.910	0.908	0.910	0.976
Melt Viscosity 70 RPM, 180° C							
Fusion Torque, mg		1885	1855	1855	1763	1865	1886
Fusion Temperature, °C		155	165	166	167	162	162
Melt Torque, mg		789	875	829	765	861	851
Energy, kJ		51.4	49	46	49.7	51	48
Fusion Time, Sec		100	142	147	114	124	146
Air Oven Aging, 2 wks. @ 125°C							
Stress @ 100% Elong., MPa		13.5	11.6	12.0	12.0	11.1	11.6
psi		1958	1682	1740	1740	1610	1682
Stress Change, %		23	4	10	19	1	7
Tensile Ultimate @ Break, MPa		27.8	25.2	23.2	25.4	26.0	24.8
psi		4027	3658	3358	3688	3771	3591
Tensile Change, %		2	3	8	10	-6	-4
Elongation @ Break, %		378	375	352	414	388	378
Elongation Change, %		-7	-3	-6	-3	-10	-10
Toughness, psi		9326	8182	7518	9305	8503	8268
Toughness Change, %		4	1	2	11	-12	-8
Hardness Duro A, pts		51	44	42	47	45	45
Hardness Change, pts		12	2	0	7	0	4
Weight Change, %		-9.1	-1.2	-1.0	-5.6	-0.7	-1.2

Table VI: Materials for Tables I-V

Material	Chemical Description	Supplier
Royalene® IM7200 EPDM	a terpolymer of ethylene, propylene and a non-conjugated diene (ENB), medium Mooney, fast curing.	Uniroyal Chemical
PDC 1280	Polypropylene	Basell
Kadox 930	Zinc Oxide	The C.P. Hall Company
Stearic acid		The C.P. Hall Company
Trigonox 145-45B-pd	2,5-bis-(tert-butylperoxy)-2,5-dimethyl-3-hexyne	Akzo Nobel
SP-1056	Halogenated Phenolic resin, substituted at paraposition	Schenectady International
SP-1045	Octylphenol heat reactive resins for rubber cure	Schenectady International
RX 13824	Dimerate Ester	The C.P. Hall Company
RX-13804	Dimerate Ester	The C.P. Hall Company
TDT	Tridecyl Tallate	The C.P. Hall Company
RX-13892	Diolelyl Dimerate	The C.P. Hall Company
DOS	Dioctyl Sebacate	The C.P. Hall Company
Sunpar 2280	Parrafinic Oil	Sun Oil Company
Sunpar 150	Parrafinic Oil	Sun Oil Company

WHAT IS CLAIMED IS:

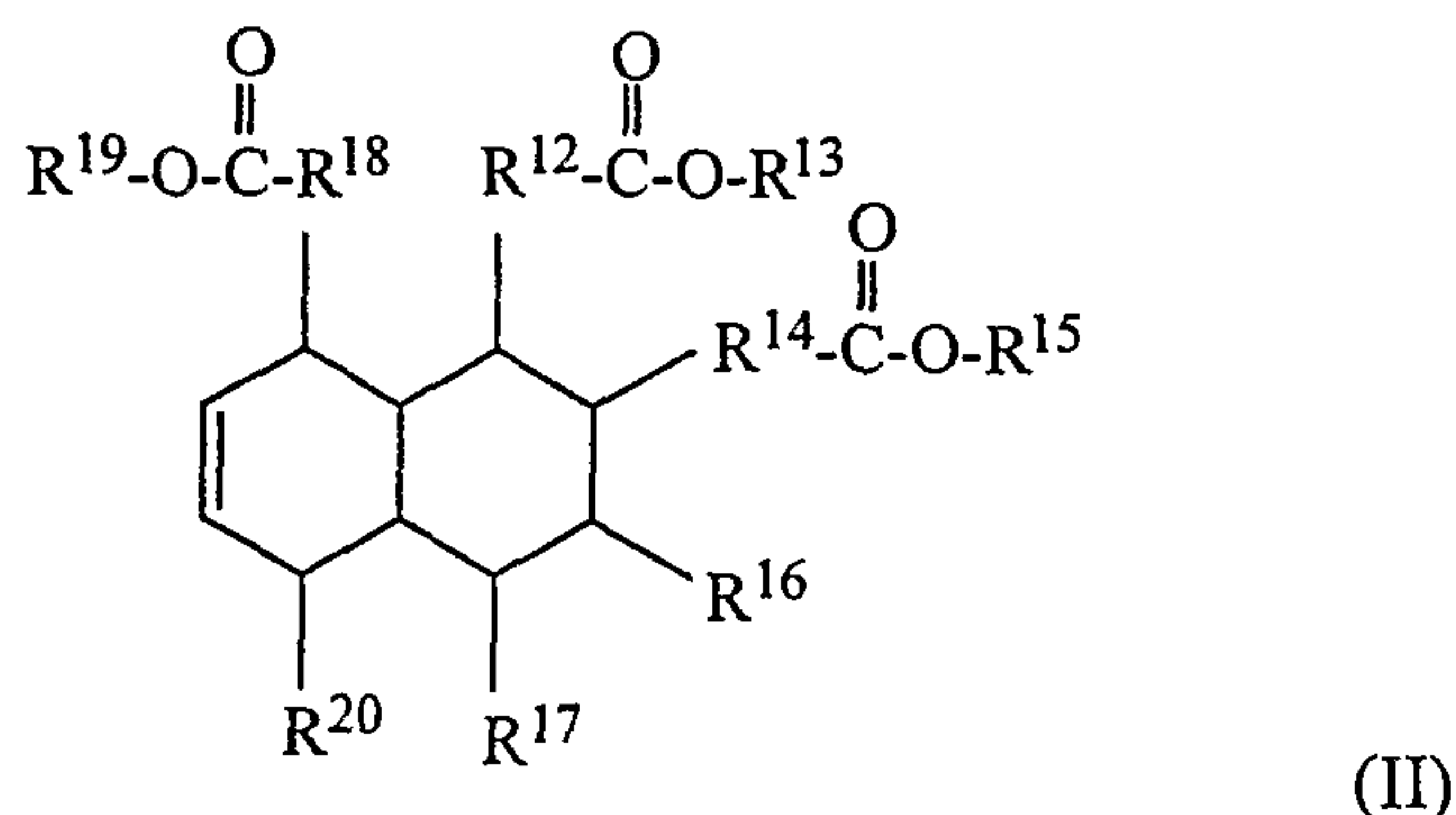
1. A plasticized thermoplastic polymer/elastomer composite composition comprising a thermoplastic polymer and a rubber selected from the group consisting of natural rubbers, synthetic rubbers, and combinations thereof, and a cyclic dimerate or trimerate ester plasticizer compound having formula I, II, or a mixture thereof:



wherein R^5 and R^7 , same or different, are a C_3-C_{24} hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

- 10 R^6 and R^8 , same or different, are a C_3-C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

- 15 R^{10} and R^{11} , same or different, are a C_3-C_{24} saturated hydrocarbon chain, straight chain or branched, or an unsaturated C_3-C_{24} hydrocarbon chain, straight chain or branched, having 1 to 6 carbon-to-carbon double bonds;



wherein R^{12} , R^{14} and R^{18} , same or different, are a C_3 - C_{24} hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

R^{13} , R^{15} and R^{19} , same or different, are a C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are a C_3 - C_{24} saturated hydrocarbon chain, straight chain or branched, or an unsaturated C_3 - C_{24} hydrocarbon chain, straight chain or branched, containing 1 to 6 carbon-to-carbon double bonds.

2. A composition in accordance with claim 1, wherein the plasticizer is selected from the group consisting of formula I, II, and a combination thereof:

wherein R^5 and R^7 are a C_6 - C_{24} hydrocarbon chain, straight chain or branched, either saturated or having 1 to 3 carbon-to-carbon double bonds;

R^6 and R^8 , same or different, are a C_3 - C_{18} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds;

R^{10} and R^{11} , same or different, are C_3 - C_{18} saturated hydrocarbon chain, straight chain or branched, or an unsaturated hydrocarbon chain, straight chain or branched, containing 1 to 3 carbon-to-carbon double bonds;

R^{12} , R^{14} and R^{18} , same or different, are a C_6 - C_{24} hydrocarbon chain, straight chain or branched, either saturated or containing 1 to 3 carbon-to-carbon double bonds;

R^{13} , R^{15} and R^{19} , same or different, are a C_3 - C_{18} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are a C_3 - C_{18} saturated hydrocarbon chain, straight chain or branched, or an unsaturated C_3 - C_{18} hydrocarbon-chain, straight chain or branched, containing 1 to 3 carbon-to-carbon double bonds.

3. A composition in accordance with claim 1, wherein the plasticizer compound having formula I, II, or a mixture thereof is present in an amount of about 0.1 parts to about 45 parts by weight, based on the combined weight of the thermoplastic polymer and rubber compounds.

5 4. A composition in accordance with claim 1, wherein the plasticizer compound having formula I, II, or a mixture thereof is present in an amount from about 5 parts to about 40 parts by weight, based on the combined weight of the thermoplastic polymer and rubber compounds.

10 5. A composition in accordance with claim 1, wherein the plasticizer compound having formula I, II, or a mixture thereof is present in an amount from about 10 parts to about 35 parts by weight, based on the combined weight of the thermoplastic polymer and rubber compounds.

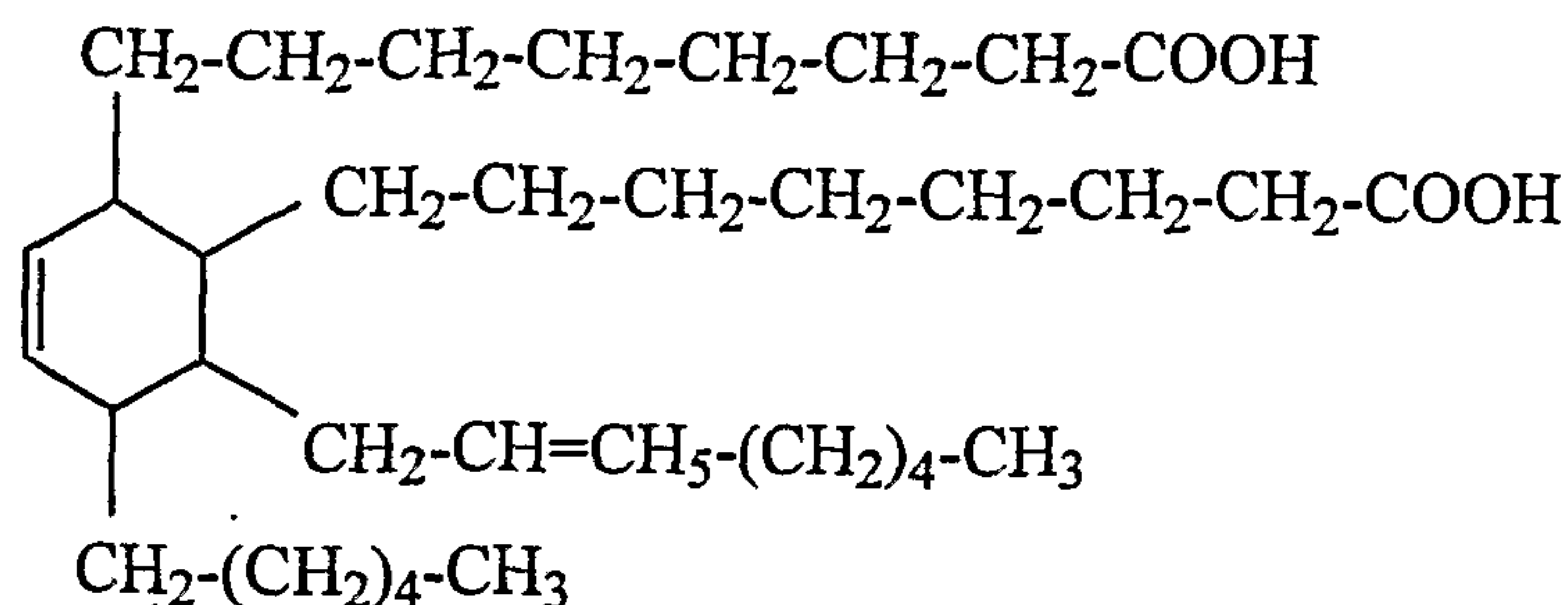
15 6. A composition in accordance with claim 1, wherein the plasticizer is an unsaturated diester formed by the reaction of a C₃₆ dimer acid and a C₃-C₁₈ alcohol, straight chain or branched, saturated, or unsaturated containing 1 to 3 carbon-to-carbon double bonds.

7. A composition in accordance with claim 6, wherein the alcohol is 2-ethylhexyl alcohol.

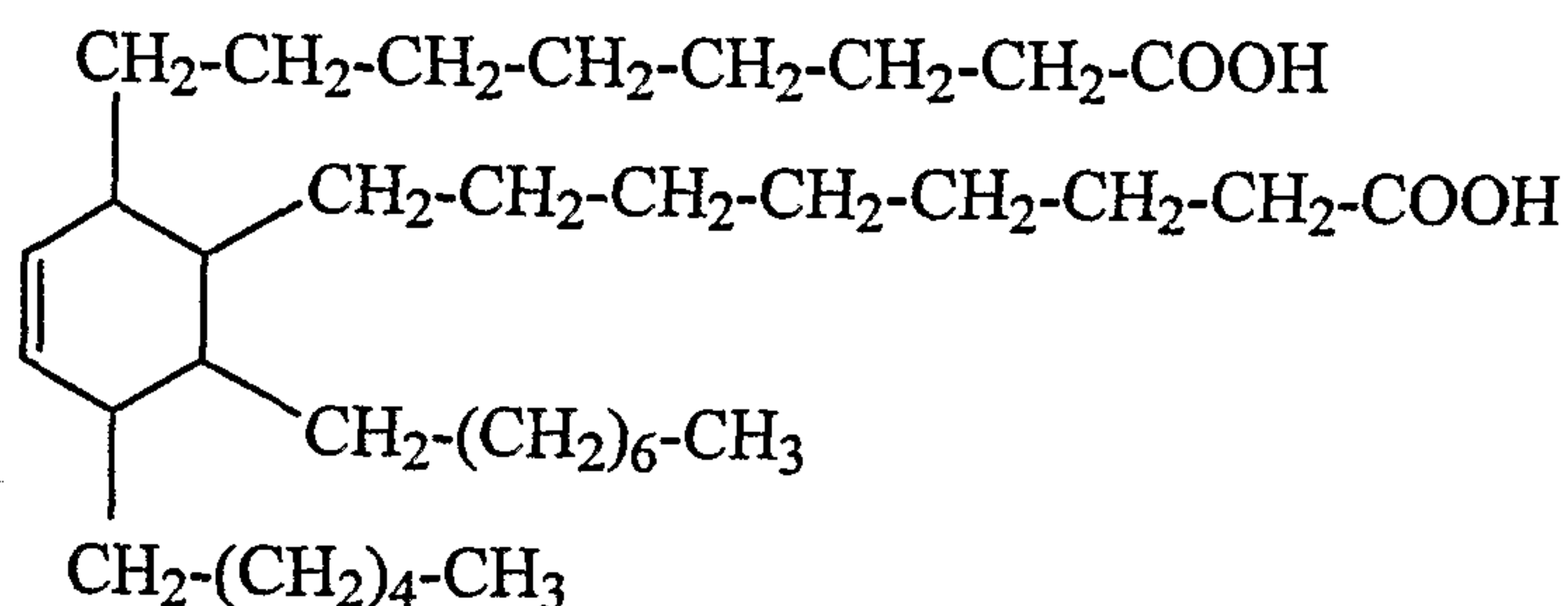
20 8. A composition in accordance with claim 6, wherein the alcohol is tridecyl alcohol.

9. A composition in accordance with claim 6, wherein the alcohol is oleyl alcohol.

10. A composition in accordance with claim 1, wherein the plasticizer comprises the following dimerate acid reacted with a C₃-C₂₄ alcohol:

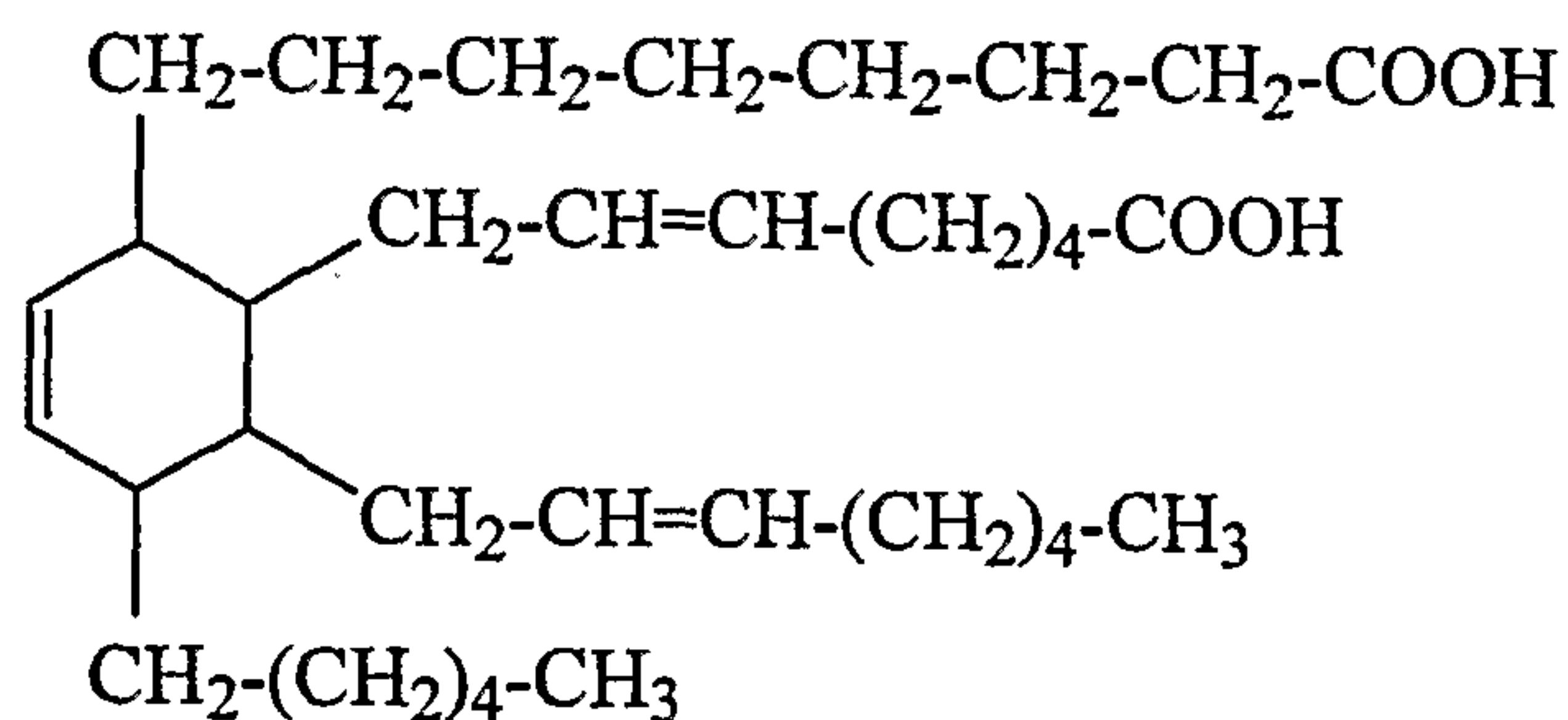


11. A composition in accordance with claim 1, wherein the plasticizer comprises the following dimerate acid reacted with a C₃-C₂₄ alcohol:



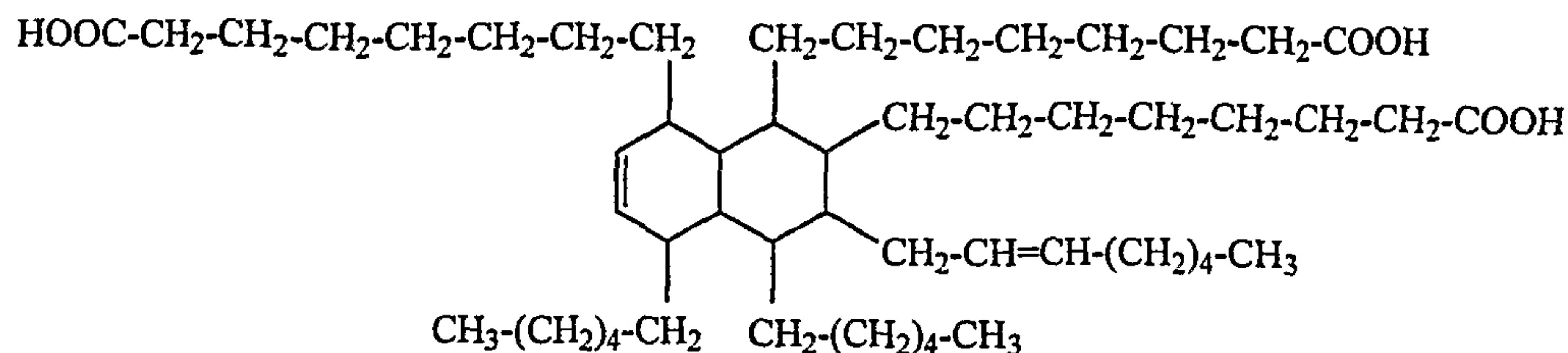
5

12. A composition in accordance with claim 1, wherein the plasticizer comprises the following dimerate acid reacted with a C₃-C₂₄ alcohol:



10

13. A composition in accordance with claim 1, wherein the plasticizer is the reaction product of a C₃-C₂₄ alcohol with a tricarboxylic acid, having the following formula:

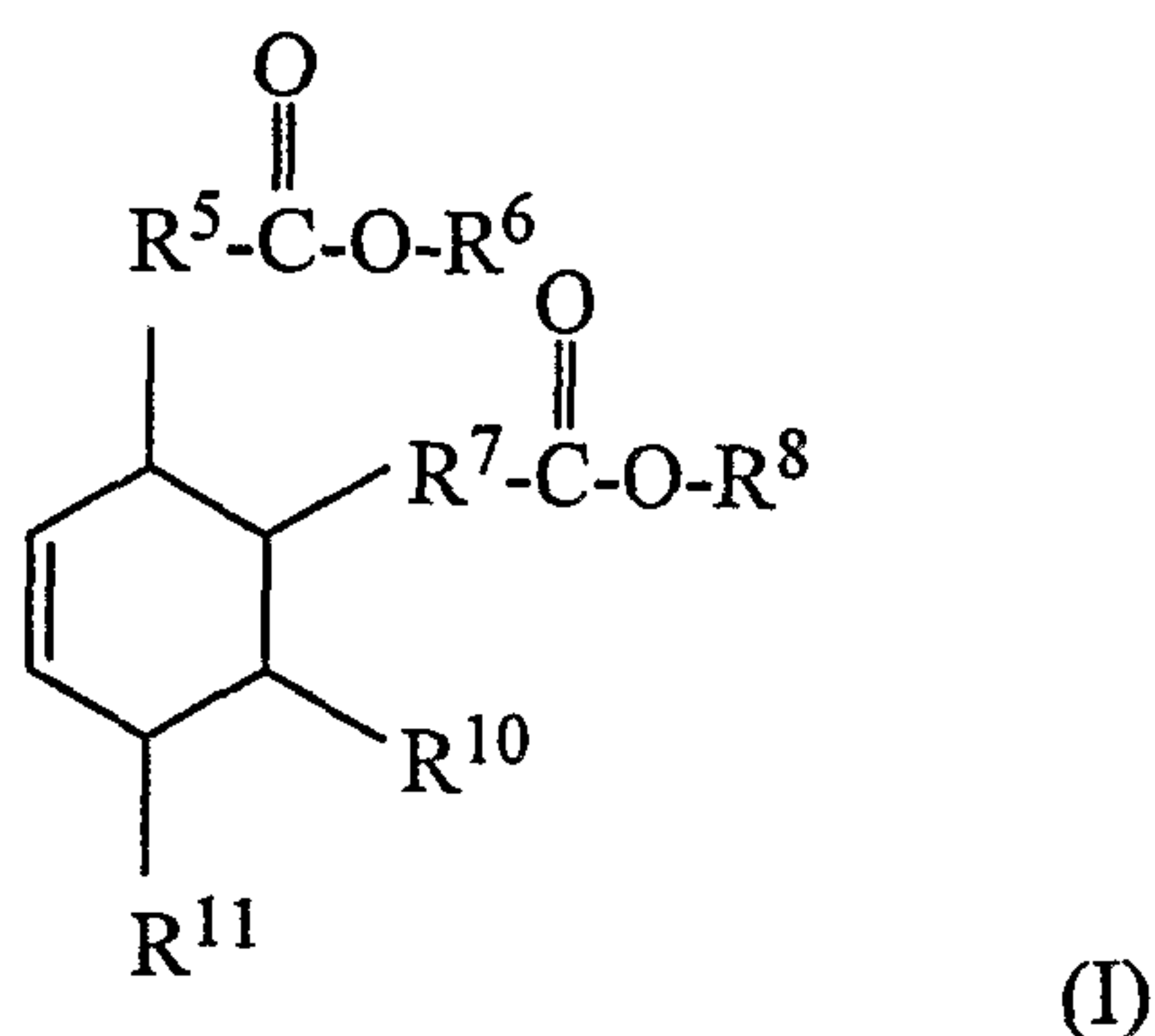


14. A composition in accordance with claim 1 wherein the plasticizer is a combination of compounds in accordance with formulas I and II.
- 5 15. A composition in accordance with claim 14, wherein the plasticizer is a reaction product of a C₃-C₂₄ alcohol straight chain or branched, saturated, or unsaturated having 1 to 3 carbon-to-carbon double bonds, with a dimer acid having CAS # 61788-89-4.
- 10 16. A composition in accordance with claim 15, wherein the alcohol is 2-ethylhexyl alcohol.
17. A composition in accordance with claim 15, wherein the alcohol is a tridecyl alcohol.
18. A composition in accordance with claim 15, wherein the alcohol is a oleyl alcohol.
- 15 19. A composition in accordance with claim 1, wherein R⁵, R⁷, R¹², R¹⁴ and R¹⁸ are fatty acid residues derived from animal or vegetable fatty acids.
- 20 20. A composition in accordance with claim 19, wherein the fatty acid residues are derived from the group consisting of butter; lard; tallow; grease; herring; menhaden; pilchard; sardine; babassu; castor; coconut; corn; cottonseed; jojoba; linseed; oiticia; olive; palm; palm kernel; peanut; rapeseed; safflower; soya; sunflower; tall; tung; and mixtures thereof.
21. A composition in accordance with claim 19, wherein the fatty acid residues are selected from the group consisting of hexanoic; octanoic; decanoic; dodecanoic; 9-dodecenoic; tetradecanoic; 9-tetradecenoic; hexadecanoic; 9-

hexadecenoic; octadecanoic; 9-octadecenoic; 9, 12-octadecadienoic; 9, 12, 15-octadecatrienoic; 9, 11, 13-octadecatrienoic; octadecatetrenoic; eicosanoic; 11-eicosenoic; eicosadienoic; eicosatrienoic; 5, 8, 11, 14-eicosatetraenoic; eicosapentaenoic; docosanoic; 13-docosenoic; docosatetraenoic; 4, 8, 12, 15, 19-
 5 docosapentaenoic; docosahexaenoic; tetracosenoic; and 4, 8, 12, 15, 18, 21-tetracosahexaenoic.

22. A composition in accordance with claim 1, further comprising a vulcanization agent.

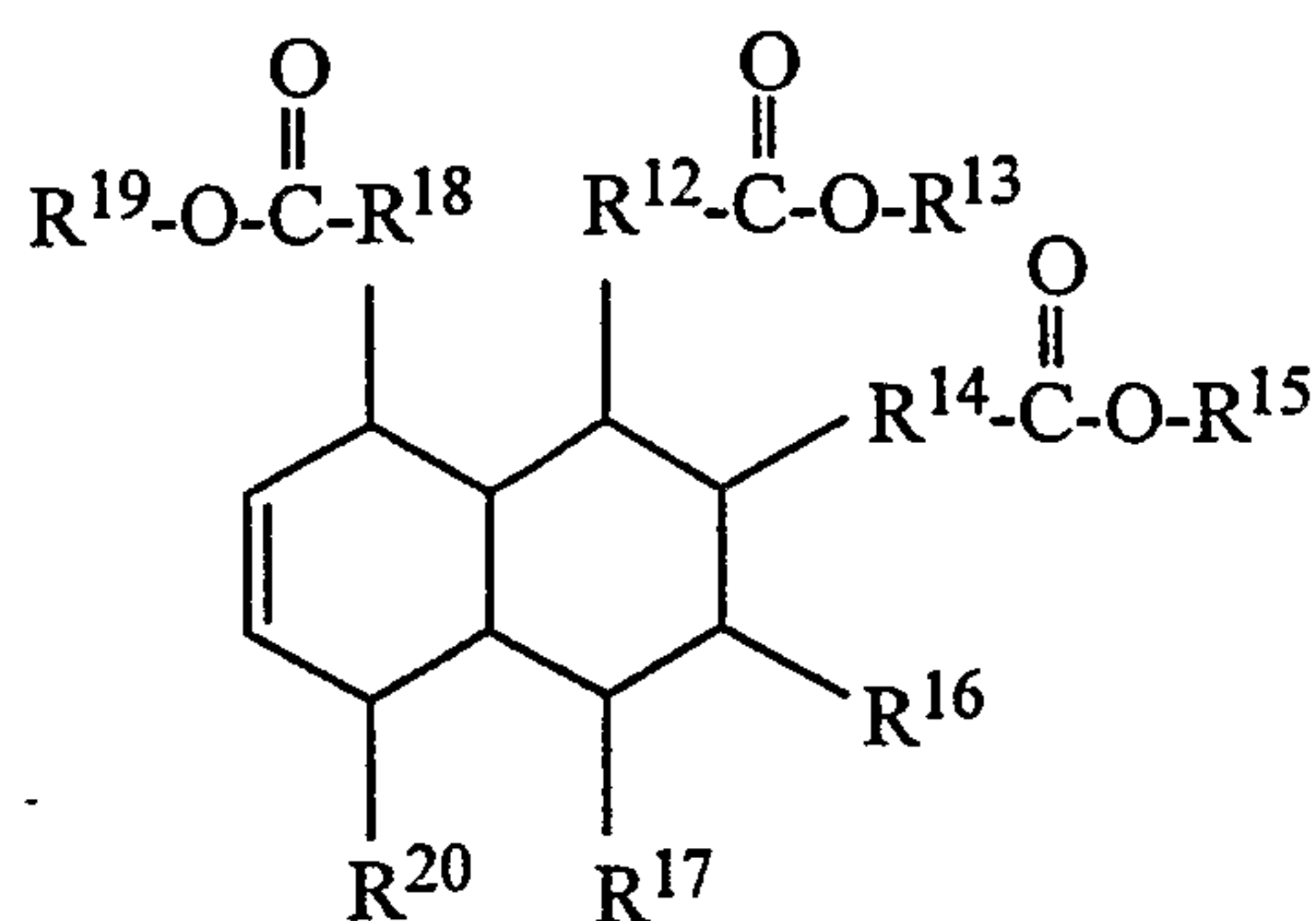
23. A method of plasticizing a composite composition including a
 10 thermoplastic polymer, a rubber selected from the group consisting of natural rubbers, synthetic rubbers and a combination thereof, and a rubber vulcanizing agent, comprising adding to said composite composition a cyclic ester plasticizer of formula I, II, or mixtures thereof:



15 wherein R^5 and R^7 , same or different, are a C_3 - C_{24} hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

R^6 and R^8 , same or different, are a C_3 - C_{24} alkyl radical, straight chain or branched; and

20 R^{10} and R^{11} , same or different, are a C_3 - C_{24} , saturated hydrocarbon chain, straight chain or branched, or an unsaturated C_3 - C_{24} , hydrocarbon chain, straight chain or branched, having 1 to 6 carbon-to-carbon double bonds;



(II)

wherein R^{12} , R^{14} and R^{18} , same or different, are a C_3 - C_{24} hydrocarbon chain, straight chain or branched, either saturated or having 1 to 6 carbon-to-carbon double bonds;

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R^{13} , R^{15} and R^{19} , same or different, are a C_3 - C_{24} alkyl radical, straight chain or branched, saturated or unsaturated containing 1 to 3 carbon-to-carbon double bonds; and

R^{16} , R^{17} and R^{20} , same or different, are a C_3 - C_{24} saturated hydrocarbon chain, straight chain or branched, or unsaturated C_3 - C_{24} hydrocarbon chain, straight chain or branched, containing 1 to 6 carbon-to-carbon double bonds.

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24. The method of claim 23, wherein the cyclic ester plasticizer is added in an amount from about 0.1 parts to about 45 parts by weight, based on the combined weight of the thermoplastic polymer and rubber compounds.

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25. The method of claim 23, wherein the cyclic ester plasticizer is added in an amount from about 5 parts to about 40 parts by weight, based on the combined weight of the thermoplastic polymer and rubber compounds.

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26. The method of claim 23, wherein the cyclic ester plasticizer is added in an amount from about 10 parts to about 35 parts by weight, based on the combined weight of the thermoplastic polymer and rubber compounds.