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<p>(21) International Application Number: PCT/US90/04573 (22) International Filing Date: 14 August 1990 (14.08.90) (30) Priority data: 395,386 17 August 1989 (17.08.89) US (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventors: KRUTAK, James, John ; 6305 Booth Court, Kingsport, TN 37663 (US). WEAVER, Max, Allen ; 125 Hill Road, Kingsport, TN 37664 (US). COATES, Clar- ence, Alvin ; Route 13, Kingsport, TN 37664 (US). HIL- BERT, Samuel, David ; Route 7, Jonesborough, TN 37659 (US). OLDFIELD, Terry, Ann ; 681 Big Ridge Road, Kingsport, TN 37660 (US). PARHAM, William, Whitefield ; 1917 Hermitage Drive, Kingsport, TN 37664 (US). PRUETT, Wayne, Payton ; 101 Walton Court, Kingsport, TN 37663 (US).</p>		<p>(74) Agent: THOMSEN, J., Frederick; 343 State Street, Ro- chester, NY 14650-2201 (US). (81) Designated States: AT (European patent), AU, BE (Euro- pean patent), CA, CH (European patent), DE (Euro- pean patent)*, DK (European patent), ES (European pa- tent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>Without international search report and to be republished upon receipt of that report.</i></p>
<p>(54) Title: ULTRAVIOLET LIGHT-ABSORBING COMPOUNDS AND SUNSCREEN FORMULATIONS AND POLYM- ERIC MATERIALS CONTAINING SUCH COMPOUNDS OR RESIDUES THEREOF</p> $R^1 - \overset{R^2}{\underset{ }{C}} = CH - A - Z - L - Z - A - CH = \overset{R^2}{\underset{ }{C}} - R^1 \quad (I)$ <p>(57) Abstract</p> <p>Disclosed are certain poly-methine compounds having formula (I), wherein each R¹ is independently selected from cyano; carboxy; alkenyloxycarbonyl; an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxy carbonyl radical; an unsubstituted or substituted, carbocyclic or heterocyclic aryl radical; an unsubstituted or substituted alkanoyl, cycloalkanoyl or aroyl radical; an unsubstituted or substituted carbamoyl radical; or an unsubstituted or substituted alkyl-sulfonyl, cycloalkylsulfonyl or arylsulfonyl radical; each R² is independently selected from cyano or an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxy carbonyl radical; each A is independently selected from an unsubstituted or substituted 1,2-phenylene or 1,2-naphthylene radical; each Z is independently selected from -O- or -S-; and L is an organic linking group bonded by non-oxo carbon atoms to each Z atom. Also disclosed are sunscreen formulations and polymeric compositions containing at least one of the poly-methine compounds or the reactive residue thereof.</p>		

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- 1 -

ULTRAVIOLET LIGHT-ABSORBING COMPOUNDS AND
SUNSCREEN FORMULATIONS AND POLYMERIC MATERIALS
CONTAINING SUCH COMPOUNDS OR RESIDUES THEREOF

5 This invention pertains to certain novel poly-
methine compounds which exhibit unique ultraviolet light
absorbing properties. This invention also concerns
polymer compositions containing at least one of the
poly-methine compounds which are useful for protecting
10 various substrates from the deleterious effects of
ultraviolet light.

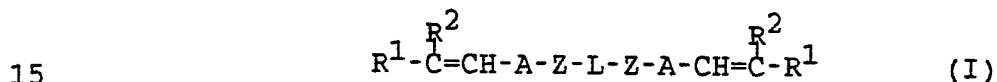
 Recently, considerable attention has been given to
the observed increase in skin cancer attributed in part
to people's lifestyles and leisure activities that
15 result in excessive and prolonged exposure to harmful
ultraviolet (UV) light rays present in solar radiation.
The UV rays have been divided into three regions:
UV-A Region (320-400 nm), UV-B Region (290-320 nm) and
UV-C Region (200-290 nm). The UV-C Region has the
20 highest energy and most damaging radiation, but is
largely absorbed by the ozone layer. UV light in the
UV-B Region, also called the Erythematous or Burning
Region, causes sunburn and is responsible for most of
the immediate damage to the human body, i.e., skin and
25 hair. UV-A radiation, also called the Tanning Region,
causes tanning but also may cause reddening of the skin
and sunburn upon prolonged exposure.

 Traditionally, sunscreen formulations have
contained UV light-absorbing chemicals capable of
30 absorbing most of the UV-B light, which is the most
likely to cause severe sunburn. Recently, to achieve a
greater degree of protection, formulations have included
a combination of UV-A and UV-B light absorbing
compounds. See, for example, N. A. Shaath, *Cosmetics*
35 and *Toiletries*, 101, March 1986, PP 55-70 and *Consumer*

- 2 -

Reports, June 1988, pp 370-374. These formulations have been designed to absorb most of the UV light in the range of 280 to 400 nm, particularly in the 280 to 360 nm range which contains the most damaging UV light.

5 The novel poly-methine compounds provided by this invention absorb UV light over a wide range of wavelengths, e.g., 280 to 400 nm, which renders them suitable for use in formulating various products that provide protection from the damaging rays present in
10 sunlight and, also, in fluorescent light. The poly-methine compounds of our invention have the formula



wherein

each R^1 is independently selected from cyano; carboxy; alkenyloxycarbonyl; an unsubstituted or
20 substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical; an unsubstituted or substituted, carbocyclic or heterocyclic aryl radical; an unsubstituted or substituted alkanoyl, cycloalkanoyl or aroyl radical; an unsubstituted or substituted
25 carbamoyl radical; or an unsubstituted or substituted alkylsulfonyl, cycloalkylsulfonyl or arylsulfonyl radical;

each R^2 is independently selected from cyano or an unsubstituted or substituted alkoxy carbonyl,
30 cycloalkoxy carbonyl or aryloxycarbonyl radical;

each A is independently selected from an unsubstituted or substituted 1,2-phenylene or 1,2-naphthylene radical;

each Z is independently selected from -O- or -S-;
35 and

L is an organic linking group bonded by non-oxo carbon atoms to each Z atom.

- 3 -

The described poly-methine compounds have been found to exhibit two strong absorption bands of almost equal intensity, a characteristic which renders the compounds particularly effective in absorbing UV light over an extended wavelength range. This absorption renders the compounds unique since prior art compounds derived from p-hydroxybenzaldehyde and various active methylene compounds such as cyanoacetic acid esters, for example those disclosed in U.S. Patents 3,706,700, 4,617,374, 4,707,537, 4,749,773 and 4,749,774, exhibit only one major absorption band, which results in their absorbing UV light over a limited range. Cinnamic acid derivatives, such as alkyl p-alkoxycinnamates, are known to be useful UV-B absorbers, having an absorption maximum in the 300 to 310 range, for sunscreen preparations.

The two major absorption bands exhibited by our novel compounds are particularly advantageous since those bands correspond roughly to the UV-A and UV-B regions of the UV spectrum. This allows formulation of sunscreen preparations which absorb most of the UV light over the range of 290 to 400 nm using only one active UV light-absorbing ingredient. Since currently available sunscreen products may cause skin sensitization and allergic reactions, a particularly valuable embodiment of our invention includes polymeric compositions, e.g., polyesters, having reacted therewith or copolymerized therein at least one compound of formula (I) which contains one or more reactive groups. These polymeric compositions are not readily absorbed through the stratum corneum layer of the skin and thus contact of the UV light-absorbing agent with the epidermis is prevented or reduced substantially.

The polymer compositions provided by this invention comprise a condensation polymer such as ester-containing

- 4 -

5 polymers, including polycarbonates and, especially,
polyesters, (1) having physically admixed therein one or
more of the poly-methine compounds of formula (I) and
(2) having reacted therewith or copolymerized therein
10 the residue of at least one of the compounds of
formula (I). Certain of the polymer compositions may be
used, as mentioned above, as UV light absorbers in
sunscreen preparations. The polymer compositions also
may be used in the preparation of coatings, film and
15 sheet material for protecting substrates from UV light.
For example, sheet material fabricated from the polymer
compositions of our invention may be used in the
manufacture of articles designed to protect the eyes
from excessive exposure to UV radiation.

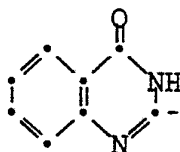
15 The polymer compositions of this invention also may
be used in the manufacture of containers suitable for
packaging a variety of materials. Many products such as
certain fruit juices, condiments, beverages, food
products, cosmetics and shampoos are affected
20 deleteriously, i.e., degraded, by UV radiation from
natural sunlight or from artificial sources such as
fluorescent lighting. In most cases these photochemical
reactions are dependent on the wavelength of the
radiation and generally increase significantly with
25 radiation of decreasing wavelength. UV radiation in the
range of 290 to 380 nm is the most damaging. Thus, as
the absorption by the packaging material of this portion
of the spectrum increases, the less the degradation of
UV-sensitive products contained therein will be. The
30 compounds of formula (I) or residues thereof
advantageously absorb a substantial portion of such
damaging UV radiation, even when used in low
concentrations, and are stable under the conditions,
e.g., the high temperatures, at which the condensation
35 polymers are manufactured and/or processed.

- 5 -

With reference to formula (I), the alkyl and alkoxy moieties of the groups recited in the definitions of R^1 and R^2 can be unsubstituted or substituted alkyl and alkoxy of up to 24 carbon atoms. Hydroxy, alkoxy, hydroxyalkoxy, halogen, alkanoyloxy, alkoxy-carbonyl, cyano, carbamoyl, aryl, aryloxy, cycloalkyl, cycloalkoxy, alkylthio, arylthio, hydroxyalkylthio, alkanoylamino, aroylamino, alkylsulfonamido, arylsulfonamido, succinimido, phthalimido and the heterocyclic groups set forth below are examples of the substituents which may be present on the substituted alkyl groups and alkoxy moieties which R^1 and R^2 can represent. The cycloalkyl moieties of the groups recited in the definitions of R^1 and R^2 can be unsubstituted cycloalkyl of 5 to 7 carbon atoms which may be substituted with alkyl or any of the substituents mentioned hereinabove. The carbamoyl groups which R^1 can represent may be unsubstituted or substituted carbamoyl such as N-alkylcarbamoyl, N,N-dialkylcarbamoyl, N-cycloalkylcarbamoyl, N-alkyl-N-cycloalkylcarbamoyl, N-arylcarbamoyl, N-alkyl-N-arylcarbamoyl and the like.

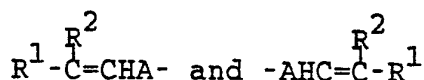
The aryl moieties of the groups recited in the definitions of R^1 and R^2 can be unsubstituted or substituted carbocyclic aryl containing 6 to 12 carbon atoms or unsubstituted or substituted heterocyclic aryl containing 5 to 10 ring atoms. Examples of the substituents which may be present on the aryl groups include alkyl and the substituents set forth in the preceding paragraph. Pyrrolyl, pyridyl, pyrimidyl, 2-benzothiazolyl, 2-benzoxazolyl, 2-benzimidazolyl, 2-thienyl, 2-furanyl, 1,3,4-thiadiazol-2-yl, 1,2,4-thiadiazol-5-yl and groups having the structure:

- 6 -



5
10 are examples of the unsubstituted aromatic heterocyclic residues which each R^2 may represent.

15 The 1,2-phenylene and 1,2-naphthylene residues represented by A can be unsubstituted or substituted, for example, with alkyl, cycloalkyl, aryl, alkoxy, halogen, etc. Further descriptions and examples of the methine residues

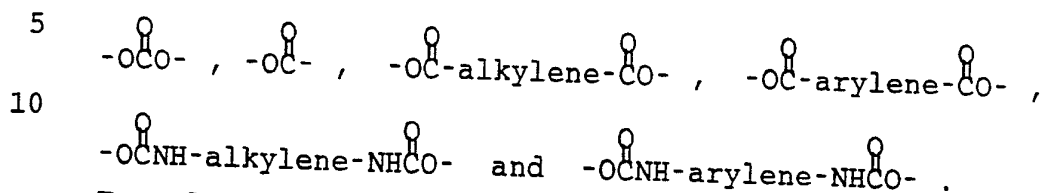


25 of the poly-methine compounds of formula (I) are set forth in U.S. Patents 4,338,247, 4,340,718, 4,617,374 and 4,661,566, the disclosures of which are incorporated herein by reference. Phenylene and
30 methylene residues A are bonded to the methine residues at the 1-position and to oxygen or sulfur atoms Z at the 2-position.

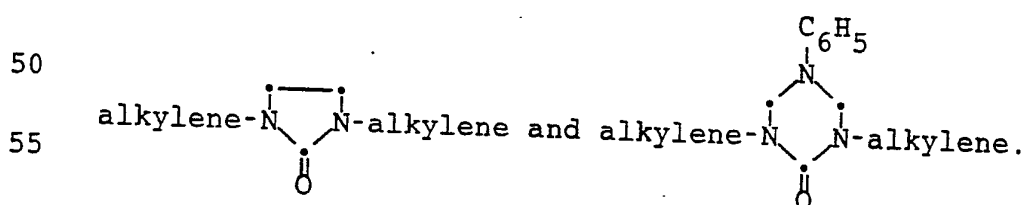
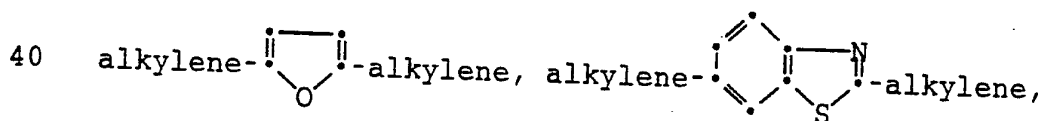
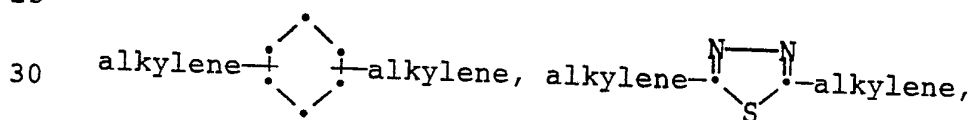
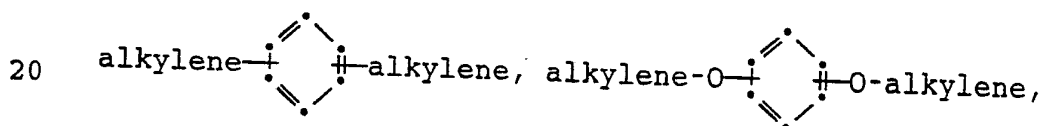
The organic linking group represented by L is bonded to the adjacent oxygen or sulfur atoms (atoms
35 represented by Z) through non-oxo carbon atoms, i.e., atoms Z are bonded directly to non-carbonylic carbon atoms, e.g., unsubstituted or substituted methylene groups, a methyldene group and an unsubstituted methylene group or a nuclear carbon atom
40 of a carbocyclic or heterocyclic aromatic group. Thus, linking group L is selected from a wide variety of alkylene, alkenylene, alkynylene, cycloalkylene, carbocyclic and heterocyclic arylene and combinations of such divalent groups. The alkylene linking groups
45 may contain within their main chain hetero atoms, e.g., oxygen, sulfur, sulfonyl, nitrogen, substituted nitrogen, and/or cyclic groups such as cycloalkylene,

- 7 -

carbocyclic arylene, divalent aromatic heterocyclic groups or ester moieties such as

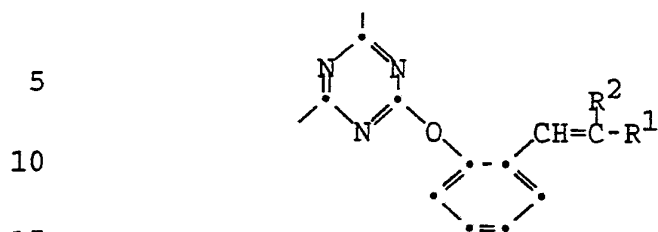


Examples of alkylene linking groups containing a cyclic moiety in the linking chain include:



60 The carbocyclic groups may be cycloalkylene such as 1,2-, 1,3- and 1,4-cyclohexylene, 1,2-, 1,3- and 1,4-phenylene and 2,6- and 2,7-naphthylene. Examples of the divalent heterocyclic groups include
 65 unsubstituted and substituted triazines such as 1,3,5-triazin-2,4-diyl, 6-methoxy-1,3,5-triazin-2,4-diyl and the group having the structure:

- 8 -



wherein R^1 and R^2 are defined hereinabove; diazines such as 2,4-pyrimidindiyl, 6-methyl-2,4-pyrimidindiyl, 6-phenyl-2,4-pyrimidindiyl, 3,6-pyridazindiyl and 2-methyl-3-oxo-4,5-pyridazindiyl; dicyanopyridines such as 3,5-dicyano-2,6-pyridindiyl and 4-phenyl-3,5-cyano-2,6-pyridindiyl; quinolines and isoquinolines such as 2,4-quinolindiyl and 2,8-isoquinolinediyl; quinoxalines such as 2,3-quinoxalindiyl; and azoles such as 2,5-thiazoldiyl, 5-methylene-2-thiazolyl, 3,5-isothiazoldiyl, 5-methylene-3-isothiazolyl, 1,3,4-thiadiazol-2,5-diyl, 1,2,4-thiadiazol-3,5-diyl, 2,6-benzothiazoldiyl, 2,5-benzoxazoldiyl, 2,6-benzimidazoldiyl, 6-methylene-2-benzothiazolyl and the group having the structure:

20

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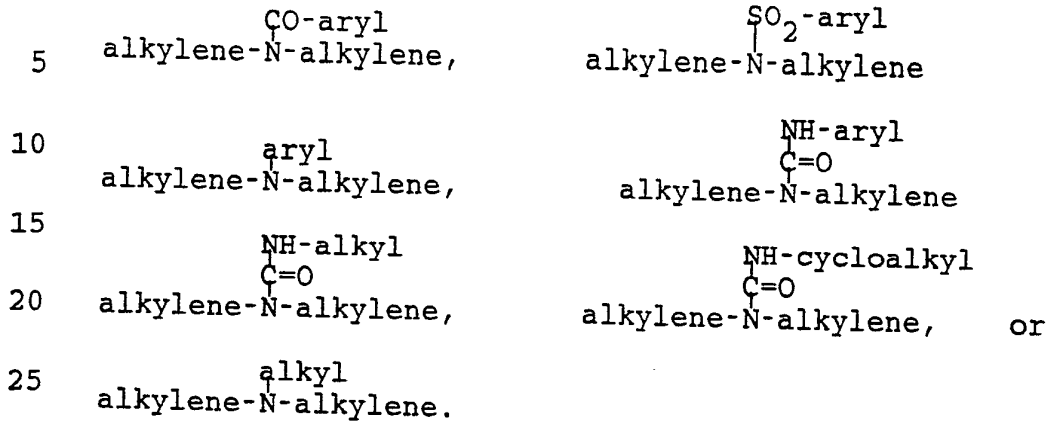
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40 and maleimides such as 1-methyl-3,4-maleimidediyl and 1-phenyl-3,4-maleimidediyl. The acyclic moieties of the linking group represented by L also may be substituted, for example, with hydroxy, alkoxy, halogen, alkanoyloxy, cyano, alkoxy-carbonyl, aryl, aryloxy, cycloalkyl, etc. The cyclic moieties of linking group L may be substituted with alkyl as well as with the substituents already mentioned. In addition to the possible substitution described above, the nitrogen atom of the nitrogen containing alkylene groups may be substituted, for example, with alkyl, aryl, alkanoyl, aroyl, alkylsulfonyl, or carbamoyl, e.g.,

45

50



30 The poly-methine compounds which may be reacted with or copolymerized in a condensation polymer to obtain one embodiment of our novel polymer compositions must bear or contain at least one substituent that is reactive with one of the monomers from which the

35 condensation polymer is derived. Examples of such reactive substituents include carbonyl halides such as carbonyl chloride, carboxy, alkoxy-carbonyl, alkenyl-oxycarbonyl, cycloalkoxy-carbonyl, aryloxy-carbonyl, amino, hydroxy, esterified hydroxy, i.e., acyloxy,

40 groups such as carboxylic acid esters, e.g., alkanoyloxy, cycloalkanoyloxy and aroyloxy, carbamic acid esters, e.g., N-alkyl-carbamoyloxy and N-aryl-carbamoyloxy and carbonate esters, e.g., ethoxy-carbonyloxy. The poly-methine residue may be

45 incorporated into or on the polymer chain by reacting one or more poly-methine compounds of formula (I) with the monomers, with a prepolymer or with the final polymer. As those skilled in the art will appreciate, when the reactive substituent or substituents are

50 alkoxy-carbonyl, alkenyloxy-carbonyl, cycloalkoxy-carbonyl, aryloxy-carbonyl, or acyloxy, the alkyl, alkenyl, cycloalkyl and aryl residues and the acid residues of the acyloxy substituents are displaced or removed from

- 10 -

the poly-methine compound upon reaction with the polymer or polymer precursor.

The preferred poly-methine compounds of our invention are those wherein

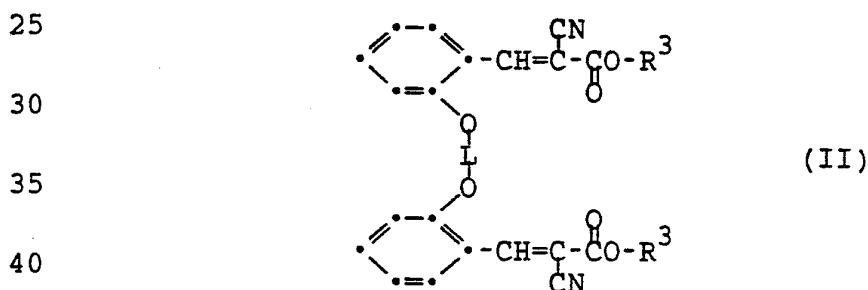
5 R^1 is an unsubstituted or substituted alkoxy-carbonyl, cycloalkoxycarbonyl or aryloxy-carbonyl radical containing up to 20 carbon atoms;

R^2 is cyano;

A is unsubstituted 1,2-phenylene;

10 Z is -O-; and

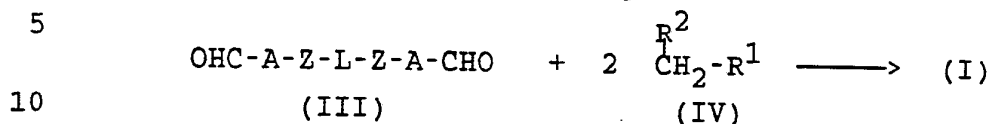
L is alkylene of up to 12 carbon atoms, 2-hydroxy-1,3-propanediyl, 2-methyl-1,3-propanediyl, oxy-bis-ethylene, i.e., $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$, oxy-bis-1,4-butanediyl, sulfonyl-bis-ethylene, thio-bis-ethylene, 15 1,2-, 1,3- and 1,4-phenylene-bis-methylene, 1,2-, 1,3- and 1,4-phenylene-bis-ethylene, 1,4-cyclohexylene-bis-methylene, 1,2-, 1,3- and 1,4-phenylene-bis-(oxyethylene), i.e., $-\text{CH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2-$, methylsulfonylimino-bis-ethylene, 20 phenylimino-bis-ethylene, acetylimino-bis-ethylene, phenylcarbonylimino-bis-ethylene and 1,2-, 1,3- and 1,4-phenylene. The poly-methine compounds which are particularly preferred have the formula



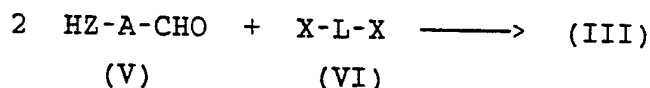
45 wherein R^3 is alkyl of up to 20 carbon atoms and L is alkylene of 2 to 8 carbon atoms, 1,2-, 1,3- or 1,4-phenylenedimethylene or 1,2-, 1,3- or 1,4-phenylenediethylene.

- 11 -

The poly-methine compounds provided by this invention may be prepared according to known procedures by reacting aldehydes (III) with active methylene compounds (IV) under Knoevenagel conditions:



Aldehydes (III) may be obtained by reacting arylaldehydes (V) with dialkylating agents (VI) using published procedures for the preparation of ethers:



wherein A, Z and L are defined hereinabove and X is halogen, especially chloro or bromo, or an organic sulfonate group, especially methylsulfonyloxy. In general, the dialkylating compounds (VI) may be prepared by reacting the corresponding diol, HO-L-OH, with a hydrohalic acid or an organic sulfonyl halide such as methylsulfonyl chloride, benzenesulfonyl bromide and toluenesulfonyl chloride.

The preparation of the poly-methine compounds is further illustrated by the following examples.

EXAMPLE 1

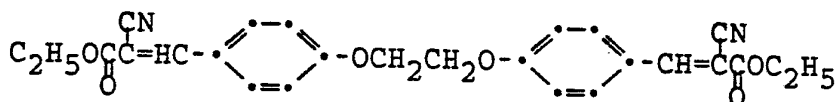
Salicylaldehyde (29.7 g, 0.243 mol), 1,2-dibromoethane (22.9 g, 0.122 mol), water (200 mL) and 50 percent aqueous sodium hydroxide (19.5 g, 0.244 mol) are mixed and heated with stirring at 90 to 95°C under nitrogen for about 24 hours. The reaction mixture is then cooled and the pH is adjusted to 9. The product is collected by filtration, washed with water and then isopropanol and dried in air to yield crude 2,2'-[(1,2-ethanediyl)bis(oxy)]-bis[benzaldehyde]. The crude product is mixed with isopropanol and the mixture is heated for 20 minutes and then cooled. The product is again collected by filtration, washed with isopropanol

- 12 -

and air dried to give 16.2 g of product. A 12.5 g portion of the product is purified further by heating to boiling in methanol (250 mL) and then filtered hot to remove a small amount of a black residue. Upon cooling the filtrate, the product precipitates and is collected by filtration and air dried to yield 6.37 g of purified product having a melting point of 126-128°C. The identity of the compound thus produced is confirmed by mass spectrometry analysis.

A mixture of 2,2'-[(1,2-ethanediyl)bis(oxy)]-bis[benzaldehyde] (2.70 g, 0.01 mol), methyl cyanoacetate (2.0 g, 0.02 mol), methanol (25 mL) and piperidine acetate (70 mg) is heated at reflux for about 2 hours and then cooled. The solid material thus formed is collected by filtration, washed with methanol and dried in air. A yield of 3.95 g, 91.4% of theory, of dimethyl 3,3'-[(1,2-ethanediyl)bis(oxy)]bis[2,1-(phenylene)]bis[2-cyano-2-propenoate] melting at 194-196°C is obtained. Mass spectroscopy confirms the structure of the product which exhibits absorption maxima at 296 nm ($\epsilon = 23,400$) and 349 nm ($\epsilon = 19,232$) in methylene chloride.

The analogous 1,4-isomer having the structure



exhibits a single absorption maximum at 343 nm in methylene chloride.

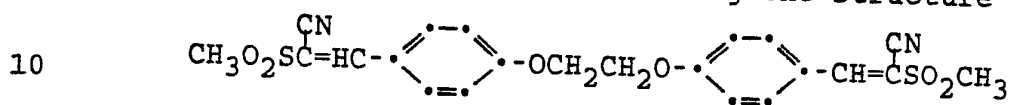
EXAMPLE 2

A mixture of 2,2'-[(1,2-ethanediyl)bis(oxy)]-bis[benzaldehyde] (2.70 g, 0.01 mol), methylsulfonyl-acetonitrile (2.38 g, 0.02 mol), methanol (30 mL) and piperidine acetate (50 mg) is heated with stirring at reflux for 2 hours. The reaction mixture is then cooled and the product is collected by filtration, washed with methanol and air dried. A yield of 4.07 g

- 13 -

(86.2% of theory) of 3,3'-[(1,2-ethanediyl)bis(oxy)2,1-(phenylene)]bis[2-(methylsulfonyl)-2-propenenitrile] melting at 235-238°C is obtained. This poly-methine compound exhibits absorption maxima at 296 nm ($\epsilon =$
 5 23,935) and at 349 ($\epsilon = 16,992$) in methylene chloride.

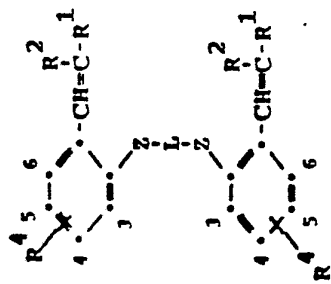
The analogous 1,4-isomer having the structure



15 exhibits a single absorption maximum at 340 nm in methylene chloride.

Additional examples of the poly-methine compounds provided by this invention are set forth in Tables I and II. The compounds may be prepared according to the procedures described above and conform to formulas
 20 given for each table.

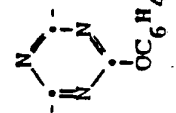
TABLE I



Example	R ¹	R ²	R ⁴	Z	L
3	-COOC ₂ H ₅	-CN	H	O	-CH ₂ CH ₂ -
4	-COOCH ₂ CH(C ₂ H ₅)(CH ₂) ₄ H	-CN	H	O	-CH ₂ CH ₂ -
5	-COO(CH ₂) ₄ H	-CN	H	O	-(CH ₂) ₄ -
6	-COO(CH ₂) ₁₈ H	-CN	H	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -
7	-COO(CH ₂) ₁₀ H	-CN	H	O	-CH ₂ CH ₂ SOCH ₂ CH ₂ -
8	-COO(CH ₂) ₈ H	-CN	H	O	-CH ₂ CH ₂ SO ₂ CH ₂ CH ₂ -
9	-COOC ₆ H ₈ -3,3,5-tri-CH ₃	-CN	H	O	-CH ₂ CH ₂ N(SO ₂ CH ₃)CH ₂ CH ₂ -
10	-COOC ₆ H ₉ -2-CH(CH ₃) ₂ -5-CH ₃	-CN	H	O	-CH ₂ C ₆ H ₄ -4-CH ₂ -
11	-COO(CH ₂) ₁₂ H	-CN	H	O	-CH ₂ CH ₂ OC ₆ H ₄ -4-OCH ₂ CH ₂ -
12	-COOCH ₂ CH=CH ₂	-CN	H	O	-CH ₂ CH ₂ N(C ₆ H ₅)CH ₂ CH ₂ -

Example	R ¹	R ²	R ⁴	Z	L
13	-COOCH ₂ C(CH ₃)=CH ₂	-CN	H	O	-(CH ₂) ₄ O(CH ₂) ₄ -
14	-COOCH ₂ CH ₂ O(CH ₂) ₁₀ H	-CN	H	O	-1,4-C ₆ H ₄ -
15	-COO(CH ₂) ₁₀ OH	-CN	H	O	-1,4-C ₆ H ₁₀ -
16	-COOCH ₂ CH ₂ O(CH ₂) ₄ H	-CN	H	O	-CH ₂ CH(OH)CH ₂ -
17	-COO(CH ₂) ₄ OOCCH ₃	-CN	H	O	-CH ₂ CH ₂ CH(OH)CH ₂ -
18	-COO(CH ₂) ₁₂ OOCCH ₃	-CN	H	O	-CH ₂ CH(OOC(CH ₂) ₄ H)CH ₂ -
19	-COOCH ₂ CH ₂ C ₆ H ₅	-CN	H	O	-CH ₂ CH(OOCOC ₂ H ₅)CH ₂ -
20	-COOCH ₂ C ₆ H ₁₁	-CN	H	O	-CH ₂ CH(OOC ₆ H ₁₁)CH ₂ -
21	-COOC ₆ H ₁₀ -4-C(CH ₃) ₃	-CN	H	O	$\begin{array}{c} \text{OOC} \text{C}_6\text{H}_4 \text{-4-} (\text{CH}_2)_6 \text{H} \\ \\ \text{-CH}_2\text{CHCH}_2\text{-} \end{array}$
22	-COOCH ₂ C ₆ H ₄ -4-O(CH ₂) ₁₀ H	-CN	H	O	$\begin{array}{c} \text{OOCNHC}_6\text{H}_4\text{-4-CH}_3 \\ \\ \text{-CH}_2\text{CHCH}_2\text{-} \end{array}$
23	-COO(CH ₂) ₉ H	-CN	H	O	-CH ₂ CH(OOCCH ₂ CN)CH ₂ -
24	-COO(CH ₂) ₁₉ H	-CN	H	O	-CH ₂ CH(OOCCH ₂ OH)CH ₂ -
25	-COOCH ₂ CH(OH)CH ₂ OH	-CN	H	O	-CH ₂ C(CH ₂ OH) ₂ CH ₂ -
26	-COOCH ₂ C ₆ H ₄ -4-CH ₂ OH	-CN	H	O	-CH ₂ C(CH ₃) ₂ CH ₂ -
27	-COOC ₆ H ₄ -4-C(CH ₃) ₂ CH ₂ C(CH ₃) ₃	-CN	H	O	-CH ₂ CH(CN)CH ₂ -

Example	R ¹	R ²	R ⁴	Z	L
28	-COOC ₆ H ₄ -4-O(CH ₂) ₁₀ H	-CN	H	0	COO(CH ₂) ₄ H -CH ₂ CHCH ₂ -
29	-COOCH ₂ CH ₂ NHCO(CH ₂) ₆ H	-CN	H	0	O(CH ₂) ₆ H -CH ₂ CHCH ₂ -
30	-COO(CH ₂) ₄ CN	-CN	H	0	OC ₆ H ₄ -4-C(CH ₃) ₂ CH ₂ C(CH ₃) ₃ -CH ₂ -CHCH ₂ -
31	-COOCH ₂ CH ₂ S(CH ₂) ₁₀ H	-CN	H	0	-CH ₂ CH(SO ₂ C ₆ H ₁₁)CH ₂ -
32	-COOCH ₂ CH(OOCOC ₂ H ₅)CH ₂ OOCOC ₂ H ₅	-CN	H	0	-CH ₂ CH(SO ₂ (CH ₂) ₁₈ H)CH ₂ -
33	-SO ₂ (CH ₂) ₄ H	-CN	H	0	-CH ₂ CH=CHCH ₂ -
34	-SO ₂ CH ₂ CH(CH ₃) ₂	-CN	H	0	-CH ₂ C=CCH ₂ -
35	-SO ₂ CH ₂ CH(C ₂ H ₅)(CH ₂) ₄ H	-CN	H	0	-CH ₂ CH(OH)CH(OH)CH ₂ -
36	-SO ₂ (CH ₂) ₁₈ H	-CN	H	0	-CH ₂ CH ₂ OCOCH ₂ CH ₂ -
37	-SO ₂ C ₆ H ₁₀ -3-CH ₃	-CN	H	0	-CH ₂ CH ₂ OOC(CH ₂) ₄ COOCH ₂ CH ₂ -
38	-SO ₂ CH ₂ C ₆ H ₄ -4-(CH ₂) ₆ H	-CN	H	0	-CH ₂ C ₆ H ₁₀ -4-CH ₂ -
39	-SO ₂ CH ₂ C ₆ H ₄ -4-(CH ₂) ₁₂ H	-CN	H	0	-CH ₂ CH ₂ NHCO(CH ₂) ₄ CONHCH ₂ CH ₂ -
40	-SO ₂ C ₆ H ₄ -4-O(CH ₂) ₉ H	-CN	H	0	-CH ₂ CH ₂ OOC(CH ₂) ₄ O-
41	-SO ₂ (CH ₂) ₄ OH	-CN	H	0	-CH ₂ CH ₂ OCH ₂ CH ₂ SCH ₂ CH ₂ -
42	-SO ₂ (CH ₂) ₆ H	-CN	H	0	-CH ₂ CH ₂ SC ₆ H ₄ -2-S-CH ₂ CH ₂ -

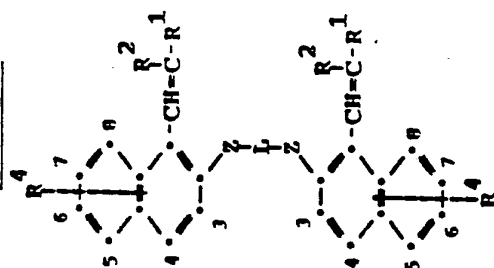
Example	R ¹	R ²	R ⁴	Z	L
43	-CONH(CH ₂) ₆ OH	-CN	H	0	$\begin{matrix} \text{SO}_2\text{C}_6\text{H}_4-3-\text{CH}_3 \\ \\ -\text{CH}_2\text{CHCH}_2- \end{matrix}$
44	-CONH(CH ₂) ₆ OOCC ₆ H ₁₁	-CN	H	0	-CH ₂ CH(OC ₆ H ₁₁)CH ₂ -
45	-CONH(CH ₂ CH ₂ O) ₂ H	-CN	H	0	-CH ₂ CH(O(CH ₂) ₁₀ H)CH ₂ -
46	-CONHCH ₂ CH ₂ OC ₆ H ₅	-CN	H	0	-CH ₂ CHClCH ₂ -
47	-CONHC ₆ H ₄ -4-O(CH ₂) ₄ H	-CN	H	0	-CH ₂ CH ₂ OC ₆ H ₄ -4-OCH ₂ CH ₂ -
48	-CONH(CH ₂) ₁₀ H	-CN	H	0	-CH ₂ CH(SC ₆ H ₄ -4-(CH ₂) ₄ H)CH ₂ -
49	-CON(CH ₃)(CH ₂) ₁₈ H	-CN	H	0	-CH ₂ CH(CH ₃)CH ₂ -
50	-CON[(CH ₂ CH ₂ O) ₂ H] ₂	-CN	H	0	-CH ₂ CH(C ₆ H ₅)CH ₂ -
51	-CON(C ₆ H ₅)CH ₂ CH ₂ OC ₂ H ₅	-CN	H	0	-CH ₂ CH(CONH ₂)CH ₂ -
52	-CON(C ₆ H ₁₁)(CH ₂) ₁₉ H	-CN	H	0	-CH ₂ CH(COO(CH ₂) ₄ H)CH ₂ -
53	-CONH(CH ₃)C ₆ H ₁₀ -4(CH ₂) ₄ H	-CN	H	0	-(CH ₂) ₆ -
54	-CONCH ₂ CH ₂ OCH ₂ CH ₂	-CN	H	0	
55	-CONCH ₂ CH ₂ N[(CH ₂) ₆ H]CH ₂ CH ₂	-CN	H	0	$\begin{matrix} \text{CN} \\ \\ -\text{CH}_2\text{CHOC}_6\text{H}_4-2-\text{CH}=\text{CCONCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2 \\ \\ \text{CH}_2- \\ (\text{CH}_2)_6\text{H} \end{matrix}$

Example	R ¹	R ²	R ⁴	Z	L
56	-CON(CH ₂) ₅	-CN	H	O	-CH ₂ CH(O(CH ₂) ₁₃ H)CH ₂ -
57	-C ₆ H ₄ -4-CN	-CN	H	O	-CH ₂ CH ₂ -
58	-C ₆ H ₄ -4-COO(CH ₂) ₄ H	-CN	H	O	-CH ₂ CH ₂ -
59	-C=N-O-C ₆ H ₄ O	-CN	H	O	-(CH ₂) ₄ -
60	-C=N-O-C ₆ H ₃ (5-COOCH ₃)O	-CN	H	O	-CH ₂ C ₆ H ₄ -4-CH ₂ -
61	-C=N-O-C ₆ H ₄ S	-CN	H	O	-(CH ₂) ₃ -
62	-C=N-O-C ₆ H ₄ NH	-CN	H	O	-CH ₂ C ₁₀ H ₆ -4-CH ₂ -
63	-C=NN=C(CH ₃)O	-CN	H	O	-CH ₂ NC(O)N(CH ₂)CH ₂
64	-C=NN=C(C ₆ H ₅)S	-CN	H	O	-CH ₂ CH ₂ OOC ₆ H ₃ -3-COOCH ₂ CH ₂ -
65	-C=CHCH=CHO	-CN	H	O	-CH ₂ C(O)CH ₂ -
66	-C=CHNH=C	-CN	H	O	-C=NC(OCH ₃)=NC=N
67	-CH=CHSCH=CH	-CN	H	O	-C=NC=NC=N CH=C(CN)-CH=CHSCH=CH
68	-C=N-O-C ₆ H ₄ C(O)NH	-CN	H	O	-CH ₂ CH ₂ -
69	-C=CH-N=CH-CH	-CN	H	O	-CH ₂ CH ₂ -

Example	R ¹	R ²	R ⁴	Z	L
70	$\overline{\text{C}=\text{CH}-\text{O}-\text{C}_6\text{H}_4-\text{N}=\text{CH}}$	-CN	H	O	$-\text{CH}_2\text{CH}_2-$
71	$-\text{COOC}_2\text{H}_5$	-CN	H	S	$-(\text{CH}_2)_4-$
72	$-\text{COOCH}_3$	-CN	H	S	$-\text{CH}_2\text{CH}_2-$
73	$-\text{COO}(\text{CH}_2)_{10}\text{H}$	-CN	H	S	$-\text{CH}_2\text{CH}_2-$
74	-CN	-CN	H	O	$-\text{CH}_2\text{CH}_2-$
75	$-\text{COC}(\text{CH}_3)_3$	-CN	H	O	$-\text{CH}_2\text{CH}_2-$
76	$-\text{COC}_6\text{H}_5$	-CN	H	O	$-\text{CH}_2\text{CH}_2-$
77	$-\text{COC}=\text{CHCH}=\text{CHS}$	-CN	H	O	$-\text{CH}_2\text{CH}_2-$
78	$-\overline{\text{C}=\text{NCH}=\text{CHS}}$	-CN	H	O	$-\text{CH}_2\text{CH}_2-$
79	$-\text{COC}_6\text{H}_4-4-\text{CN}$	-CN	H	O	$-\text{CH}_2\text{CH}_2-$
80	$-\text{COOC}_2\text{H}_5$	$-\text{COOC}_2\text{H}_5$	H	O	$-\text{CH}_2\text{CH}_2-$
81	$\overline{\text{C}=\text{N}-\text{O}-\text{C}_6\text{H}_3(5-\text{COOC}_2\text{H}_5)_2\text{O}}$	$-\text{COOC}_2\text{H}_5$	H	O	$-\text{CH}_2\text{CH}_2-$
82	$-\text{SO}_2\text{C}_6\text{H}_5$	$-\text{COOC}_2\text{H}_5$	H	O	$-\text{CH}_2\text{CH}_2-$
83	$\overline{\text{C}=\text{N}-\text{O}-\text{C}_6\text{H}_3(5-\text{COOC}_2\text{H}_5)_2\text{S}}$	$-\text{COOCH}_3$	H	O	$-\text{CH}_2\text{CH}_2-$
84	$-\text{COC}_6\text{H}_4-4-\text{OCH}_3$	$-\text{COOC}_2\text{H}_5$	H	O	$-\text{CH}_2\text{CH}_2-$
85	$-\text{COC}_6\text{H}_5$	$-\text{COOC}_2\text{H}_5$	H	O	$-\text{CH}_2\text{CH}_2-$

Example	R ¹	R ²	R ⁴	Z	L
86	-COO(CH ₂) ₈ H	-COO(CH ₂) ₈ H	H	0	-CH ₂ CH ₂ -
87	-COOCH ₂ CH ₂ OH	-COOCH ₂ CH ₂ OH	H	0	-CH ₂ CH ₂ -
88	-C ₆ H ₄ -4-COOCH ₃	-COOCH ₃	H	0	-CH ₂ CH ₂ -
89	-COOCH ₃	-CN	5-OCH ₃	0	-CH ₂ CH ₂ -
90	-COOC ₂ H ₅	-CN	5-C ₆ H ₅	0	-CH ₂ CH ₂ -
91	-COO(CH ₂) ₄ H	-CN	3,5-di-CH ₃	0	-CH ₂ CH ₂ -
92	-COOCH ₂ CH ₂ OCH ₃	-CN	5-Cl	0	-CH ₂ CH(OH)CH ₂ -
93	-CN	-CN	4-CH ₃	0	-CH ₂ CH(OH)CH ₂ -
94	-COOCH ₃	-CN	4-OCH ₃	0	-(CH ₂) ₄ -
95	-COOH	-CN	H	0	-CH ₂ CH ₂ OCH ₂ CH ₂ -
96	-COOCH ₃	-CN	5-C ₆ H ₁₁	0	-CH ₂ CH ₂ -
97	-C=NCH=CHCH=N	-CN	H	0	-CH ₂ CH ₂ -
98	-C=N-o-C ₆ H ₃ -6-[(CH ₂) ₄ H]S	-CN	H	0	-CH ₂ CH ₂ -
99	-C=N-o-C ₆ H ₃ -6-[O(CH ₂) ₄ H]S	-CN	H	0	-CH ₂ CH ₂ -

TABLE II



Example	R ¹	R ²	R ⁴	Z	L
100	-COOCH ₃	-CN	H	O	-CH ₂ CH ₂ -
101	-COOC ₂ H ₅	-CN	H	O	-(CH ₂) ₄ -
102	-COO(CH ₂) ₄ H	-CN	H	O	-(CH ₂) ₆ -
103	-COO(CH ₂) ₆ H	-CN	H	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -
104	-COO(CH ₂) ₁₀ H	-CN	H	O	-CH ₂ CH(OH)CH ₂ -
105	-COOCH ₂ CH(C ₂ H ₅)(CH ₂) ₄ H	-CN	H	O	-CH ₂ CH ₂ -
106	-COOC ₂ H ₅	-CN	H	S	-CH ₂ CH ₂ -
107	-CN	-CN	H	O	-CH ₂ C ₆ H ₄ -4-CH ₂ -

Example	R ¹	R ²	R ⁴	Z	L
108	-SO ₂ CH ₃	-CN	H	O	-CH ₂ CH ₂ OC ₆ H ₄ -4-OCH ₂ CH ₂ -
109	-SO ₂ C ₆ H ₅	-CN	H	O	-CH ₂ CH(OOCCH ₃)CH ₂ -
110	-SO ₂ C ₆ H ₁₁	-CN	H	O	-CH ₂ CH=CHCH ₂ -
111	-CONH(CH ₂) ₄ H	-CN	H	O	-CH ₂ C=CCH ₂ -
112	-CON(CH ₂ CH ₂ OH) ₂	-CN	H	O	-CH ₂ CH ₂ SCH ₂ CH ₂ -
113	-CONHC ₆ H ₅	-CN	H	O	-CH ₂ CH(O(CH ₂) ₄ H)CH ₂ -
114	-CONHC-N-O-C ₆ H ₄ S	-CN	H	O	-CH ₂ CH ₂ SO ₂ CH ₂ CH ₂ -
115	-CONHC-NN=C(SC ₂ H ₅) ₂ S	-CN	H	O	-CH ₂ C ₆ H ₁₀ -4-CH ₂ -
116	-C ₆ H ₄ -4-COOCH ₃	-CN	H	O	-CH ₂ CH(OH)CH(OH)CH ₂ -
117	-C-N-O-C ₆ H ₄ O	-CN	H	O	-CH ₂ CH ₂ OCOCH ₂ CH ₂ -
118	-C-N-O-C ₆ H ₄ S	-CN	H	O	-1,4-C ₆ H ₄ -
119	-C-NN=C(C ₆ H ₅)O	-CN	H	O	-CH ₂ C(CH ₃) ₂ CH ₂ -
120	-C-NC(CH ₃)=CHS	-CN	6-CH ₃	O	-CH ₂ CH ₂ -
121	-COC ₆ H ₅	-CN	3-OCH ₃	O	-CH ₂ CH ₂ -
122	-COC(CH ₃) ₃	-CN	6-OCH ₃	O	-CH ₂ CH ₂ -

Example	R ¹	R ²	R ⁴	Z	L
123	-CO(CH ₂) ₆ H	-CN	3,4-di-Cl	0	-CH ₂ CH ₂ -
124	-COOC ₂ H ₅	-COOC ₂ H ₅	4-Cl	0	-CH ₂ CH ₂ -
125	-C-N-O-C ₆ H ₃ (5-COOC ₂ H ₅)O	-COOC ₂ H ₅	5-OCH ₃	0	-CH ₂ CH ₂ -
126	-C ₆ H ₄ -4-COOCH ₃	-COOCH ₃	2,5-di-OCH ₃	0	-CH ₂ CH ₂ -
127	-COOH	-CN	H	0	-CH ₂ CH ₂ -
128	-COOCH ₂ CH=CH ₂	-CN	H	0	-CH ₂ CH ₂ -
129	-COOC ₆ H ₁₁	-CN	H	0	-CH ₂ CH ₂ -
130	-COOCH ₂ CH ₂ OC ₆ H ₅	-CN	H	0	-CH ₂ CH ₂ -

- 24 -

The sunscreen formulations provided by this invention include compositions comprising at least one of the poly-methine compounds of formula (I) dissolved, suspended or dispersed in a dermatologically-acceptable
5 base. For example, the poly-methine compounds may be dissolved or dispersed in mineral oil, water-ethanol, hexylene glycol, isopropyl myristate, isopropyl palmitate, poly(alkylene glycols) such as poly(propylene glycol) having a molecular weight of about 400 to 1000 and
10 various cosmetic oils such as almond, apricot kernel, avocado, castor, citrus seed, coconut cacao butter (also known as oil of theobroma), corn, cottonseed, egg, jojoba oil lanolin, linseed, mink, olive, palm, peach kernel, peanut, rapeseed, safflower, sesame, shark, soybean, turtle,
15 whale and wheat germ.

Additional types of cosmetic oils or other usable vehicles include pharmaceutical grades of synthetic oils derived from natural fatty products (such as those available from Drew Chemical Corp. under the name
20 Neobee M-5), acetylated monoglycerides (Myvacet), dimethyl phthalate, liquid paraffin, silicones, oleyl alcohols, stabilized castor oil, stabilized castor oil combined with either polyethylene glycol 400 dilaurate or triethanolamine oleate, liquid paraffin combined with
25 stabilized castor oil, stearic acid, wool alcohol, cetyl alcohol, Polawax (a polyethylene ester of sorbitan), glycerin, sodium citrate, silicon fluid such as MS200 perfume oil, water, N,N-diethyltoluamide, glyceryl monostearate, Polychol 5 (an ethoxylated lanolin alcohol
30 preparation), butylated hydroxytoluene, hydroxyethyl cellulose, and carboxymethyl cellulose, triethanolamines, light amber petrolatum, calcium stearate, kaolin, Croda liquid base, water-soluble vinyl polymers (such as available from B.F. Goodrich Chemical Co. under the name
35 Carbopol 940), Arlacel, Tween, glycerol monostearate,

- 25 -

carbowaxes, methocels, boric acid, ammonyxes, ethoxylated derivatives of lanolin and lanolin components (such as are available from American Cholesterol Products under the name Solulan 16), spermaceti, hexadecyl alcohol, surface
5 active lanolin derivatives (such as are available from American Cholesterol Products, Inc. under the name Amerchol L-101), microcrystalline wax, beeswax, borax, lanogene, acetylated lanolin, polyoxyethylene
10 oleate/laurate, polyethoxylated high molecular weight amides (such as Ethomid HT/15 from Armour Industrial Chemical Co.), polyoxyethylene ethers of higher aliphatic alcohols (such as those available from ICI under the name Brijs) and the like.

The oil solutions/dispersions may be combined with
15 surface active agents commonly used in cosmetic preparations and emulsified with water to obtain either water in oil or, preferably, oil in water emulsions. The concentration of poly-methine compound in such sunscreen formulations typically will be in the range of 0.1 to 20.0
20 weight percent and more commonly 2.5 to 10.0 weight percent, based on the total weight of the sunscreen formulation.

Another embodiment of the sunscreen formulations according to our invention comprises a polyester having
25 reacted therewith or copolymerized therein the residue of at least one of the poly-methine compounds of formula (I) wherein the poly-methine compound bears at least one and preferably two substituents that are reactive with one of the monomers from which the polyester is derived.
30 Examples of the requisite reactive groups are set forth hereinabove.

The polyesters which may be used in the preparation of the polymeric sunscreen compositions include thermoplastic, crystalline or amorphous polyesters
35 produced by conventional polymerization techniques using

- 26 -

one or more diols and one or more dicarboxylic acids or ester-forming equivalents thereof. Typically, the polyesters have a number average molecular weight of 3,000 to 50,000 and an inherent viscosity of 0.1 to 0.6, measured at 25°C using 0.5 g of polymer per 100 mL of a solvent consisting of 60 parts by weight phenol and 40 parts by weight tetrachloroethane.

The diol components of the described polyesters may be selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 1,2-, 1,3- and 1,4-cyclohexanedimethanol, 1,2-, 1,3- and 1,4-cyclohexanediol, X,8-bis(hydroxymethyl)-tricyclo-[5.5.1.0]-decane wherein X is 3, 4 or 5, and polydiols such as diethylene glycol, triethylene glycol, tetraethylene glycol, poly(ethylene glycol) having a molecular weight of 200 to 10,000, dipropylene glycol, tripropyleneglycol, tetrapropylene glycol poly(propylene glycol) having a molecular weight of 500 to 4,000 and poly(1,4-butanediol), or poly(tetramethylene glycol), having a molecular weight of 800 to 10,000. The cycloaliphatic diols may be employed as their cis or trans isomers or a mixture thereof.

The dicarboxylic acid residues of the polyesters may be derived from aliphatic, cycloaliphatic and aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 1,2-, 1,3- and 1,4-cyclohexanedicarboxylic acid, succinic acid, glutaric acid, sebacic acid, 1,12-dodecanedioic acid, 2,6-naphthalenedicarboxylic acid and the like. Either the dicarboxylic acid or ester-forming equivalents thereof such as anhydrides, acid chlorides or, especially, esters such as the dimethyl, diethyl, dipropyl and bis(2-hydroxyethyl) esters, may be used. The preferred polyesters comprise at least 50 mole percent terephthalic acid and/or 2,6-naphthalenedicarboxylic acid

- 27 -

residues and at least 50 mole percent of diols selected from ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propane-diol, 1,4-cyclohexanedimethanol or a mixture thereof. The polyester component of the
5 polymeric sunscreen compositions most preferably comprises at least 90 mole percent terephthalic and/or 2,6-naphthalenedicarboxylic acid residues and at least 90 mole percent of residues of ethylene glycol, 1,4-
10 1,4-cyclohexanedimethanol or a mixture thereof.

The concentration of the residue of the poly-methine compound of formula (I) in the polyester can be varied substantially depending, for example, on the amount of the polyester used in the sunscreen
15 composition. Concentration of 1.0 to 50.0 weight percent, based on the weight of the polyester, may be used with a concentration of 5.0 to 30.0 weight percent being preferred.

The polyester in which at least one of the
20 compounds of formula (I) has been reacted or copolymerized may be used in the preparation of sunscreen compositions by dissolving or dispersing the polyester in a cosmetically-acceptable base. If the polyester is insoluble in the cosmetic base, dispersion and
25 consequent particle size reduction can be accomplished by any of the methods practiced by those skilled in the art, including 3-roll milling using a cosmetic oil or base and surface active agents described hereinabove.

The polymer compositions provided in accordance
30 with this invention comprise a condensation polymer, e.g., casting, extrusion or molding grade polyester or polycarbonate, (1) having physically admixed therein one or more of the poly-methine compounds of formula (I) or (2) having reacted therewith or copolymerized therein the
35 residue of a least one of the compounds of formula (I).

- 28 -

This embodiment of our invention can be used in the manufacture of film, sheet material, packaging material and other shaped articles for protecting various products from UV radiation. The casting or molding grade

5 polyesters employed in this embodiment of our invention typically have an inherent viscosity of 0.4 to 1.2 and are comprised of at least 50 mole percent terephthalic acid residues, 1,4-cyclohexanedicarboxylic acid residues, 2,6-naphthalenedicarboxylic acid residues or a mixture

10 thereof and at least 50 mole percent of ethylene glycol residues, 1,4-butanediol residues, 1,4-cyclohexanedimethanol residues or a mixture thereof. Particularly preferred casting and molding grade polyesters are comprised of 75 to 100 mole percent terephthalic acid

15 residues and 75 to 100 mole percent ethylene glycol residues.

The sheet material manufactured from the aforesaid polymer compositions may be used in safety glass and eyewear including spectacles and contact lenses to

20 protect the human retina against harmful UV-A and UV-B radiation. The surface of such polyester sheet material may be coated with a UV light-cured hard coat for use in safety lens material and UV light-blocking sheeting.

Typical polycarbonates which may be used in the

25 preparation of the polymer compositions are disclosed in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Volume 28, pages 479-494, the disclosure of which is incorporated herein by reference.

The most preferred casting, extrusion and molding

30 grade polyesters which may be used in our novel polymeric compositions comprise poly(ethylene terephthalate) and poly(ethylene terephthalate) wherein up to 5 mole percent of the ethylene glycol residues have been replaced with residues derived from 1,4-

35 cyclohexanedimethanol and wherein the polyesters have

- 29 -

been sufficiently heat set and oriented by methods well known in the art to give a desired degree of crystallinity.

The concentration of the poly-methine compound or residue thereof in the casting, extrusion or molding grade condensation polymer can be varied substantially depending, for example, on the intended function of the UV-absorbing compound or residue thereof and/or the end use from which the polymer composition is designed.

When the polymer composition is to be used in the fabrication of relatively thin-walled containers, e.g., 254 to 762 microns thick, to screen UV light in the range of about 250 to 390 nm, the concentration of the poly-methine compound normally will be in the range of 50 to 1500 ppm (parts by weight per million parts by weight polymer) with the range of 200 to 800 ppm being especially preferred. For polymer compositions destined for extrusion or casting into thin film, e.g., 25 to 254 microns thick, concentrations of 1000 to 10,000 ppm of the poly-methine compound normally will be used. For example, for equivalent protection from UV light, a 178 micron-thick film will contain about 1600 ppm whereas a 51 micron-thick film will contain about 6000 ppm of at least one of the poly-methine compounds or a residue thereof.

The sunscreen formulations and polymeric compositions of our invention are further illustrated by the following examples.

EXAMPLE 131

A mixture of triethanolamine (0.50 g) in water (67.8 g) heated to 60°C is added slowly to a rapidly-stirred, 70°C, brown solution of the following ingredients:

6.0 g	Mineral oil (Exxon Primol 355);
7.0 g	Isopropyl myristate;
3.0 g	Glyceryl monostearate (Myverol 18-06);

- 30 -

- 3.0 g Propylene glycol;
3.0 g Stearic acid;
0.5 g Hexadecanol;
1.0 g Vitamin E (Eastman 6-40); and
5 8.0 g Compound of Example 4.

The mixture is stirred continuously while it cools to 40°C and when the temperature is below 40°C methyl paraben (0.05 g), propyl paraben (0.05 g) and fragrance (0.10 g, Coppertone-type) are added and the mixture is cooled to
10 room temperature. When applied to the skin, the cream has an acceptable smooth texture.

EXAMPLE 132

The following materials are placed in a 500-mL three-necked, round-bottom flask:

- 15 97 g (0.5 mol) dimethyl terephthalate
62 g (1.0 mol) ethylene glycol
0.00192 g Ti from a n-butanol solution of
acetyl-triisopropyl titanate
0.0053 g Mn from an ethylene glycol solution
20 of manganese acetate
0.0216 g Sb from an ethylene glycol solution
of antimony acetate
0.0072 g Co from an ethylene glycol solution
of cobaltous acetate

25 The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated at 200°C in a Belmont metal bath for 60 minutes and at 210°C for 75 minutes with a nitrogen sweep over the reaction mixture. Then 1.57 mL
30 of an ethylene glycol slurry of a mixed phosphorus ester composition (Zonyl A) which contains 0.012 g phosphorus is added. The temperature of the bath is increased to 230°C. At 230°C dimethyl
3,3'-[1,2-ethanediyl-bis(oxy)bis-2,1-phenylene]

- 31 -

bis[2-cyano-2-propenoate] (0.096 g, 1000 ppm) prepared in Example 1 is added to the flask. Five minutes after this addition, a vacuum with a slow stream of nitrogen bleeding in the system is applied over a five-minute
5 period until the pressure is reduced to 200 mm Hg. The flask and contents are heated at 230°C under a pressure of 200 mm Hg for 25 minutes. The metal bath temperature is increased to 270°C. At 270°C the pressure is reduced slowly to 100 mm Hg. The flask and contents
10 are heated at 270°C under a pressure of 100 mm Hg for 30 minutes. The metal bath temperature is increased to 285°C and the pressure is reduced slowly to 4.5 mm Hg. The flask and contents are heated at 285°C under pressure of 4.5 mm Hg for 25 minutes. Then the
15 pressure is reduced to 0.25 mm Hg and polycondensation is continued for 40 minutes. The flask is removed from the metal bath and is allowed to cool in a nitrogen atmosphere while the polymer crystallizes. The resulting polymer has an inherent viscosity of 0.60 measured in a
20 60/40 ratio by weight of phenol/tetrachloroethane at a concentration of 0.5 g per 100 mL. An amorphous 381 micron thick film molded from this polymer exhibits a strong absorption peak with a maximum at 357 nm.

EXAMPLE 133

25 Four hundred grams of polyethylene terephthalate (I.V.=0.71) are dry blended with 0.32 g (800 ppm) of the poly-methine compound of Example 2. The blend is dried overnight (16 hours) in a vacuum oven at 110°C. After
30 drying, the material is melt blended and extruded into 254 micron film on a C. W. Brabender 3/4 inch (1.9 cm) extruder (25 to 1 L/D). A transmission spectrum of the 254 micron film obtained using a Perkin-Elmer Lambda 6 UV/Vis Spectrophotometer shows strong absorption of light in the 300-400 nanometer wavelength range.

- 32 -

EXAMPLE 134

The following materials are placed in a 500-mL three-necked, round-bottom flask:

43.5 g (0.224 mol) dimethyl terephthalate

5 37.1 g (0.412 mol) 1,4-butanediol

0.0072 g Ti from a n-butanol solution of acetyl-triisopropyl titanate

22.0 g (0.051 mol) compound of Example 1

The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated at 200°C in a Belmont metal bath for about 2 hours and then the temperature is increased to and maintained at 220°C for 2 hours with a nitrogen sweep over the reaction mixture. After increasing the temperature to 230°C and with a stream of nitrogen bleeding into the system, vacuum is applied slowly at about 230°C until the pressure is reduced to about 0.5 to 1.0 mm Hg and the temperature is held at approximately 230°C for 10 hours. The vacuum is removed and methyl benzoate (100 mL) is added dropwise with stirring. Heating at 230°C is continued for 10-15 minutes as the polymeric composition dissolves. The hot solution then is transferred to a 2-L beaker and stirring is continued as the composition cools. When the composition becomes very viscous, n-hexane (600 mL) is added to facilitate stirring. The crystalline polymer is collected by filtration, reslurried twice in n-hexane to remove the methyl benzoate and then dried in a vacuum oven under nitrogen. A yield of 68.3 g (94.0% of theory) of a pale tan solid is obtained. The poly(1,4-tetramethylene terephthalate) obtained contains approximately 30.3 weight percent of the residues of the compound of Example 1 copolymerized therein and has an inherent viscosity of 0.337 measured at 25°C using 0.5 g polymer per 100 mL of a solvent

- 33 -

consisting of 60 parts by weight phenol and 40 parts by weight tetrachloroethane.

EXAMPLE 135

The procedure described in Example 134 is
5 duplicated except that the polycondensation step is carried out at 235°C for about 1 hour. The resulting polyester composition containing the residue of the compound of Example 1 copolymerized therein has an inherent viscosity of 0.184 measured in a 60/40 ratio by
10 weight phenol/tetrachloroethane mixture at a concentration of 0.5 g per 100 mL.

EXAMPLE 136

The following materials are placed in a 500-mL three-necked, round-bottom flask:

15 182.8 g (0.749 mol) dimethyl 2,6-naphthalene-dicarboxylate
108.0 g (1.2 mol) 1,4-butanediol
0.0225 g Ti from a n-butanol solution of acetyl-triisopropyl titanate
20 22.0 g (0.051 mol) compound of Example 1

The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath under a nitrogen sweep at 200°C for 1.75 hours, at 220°C for 1
25 hour and at 230°C for 1 hour. The reaction mixture then is heated at 240°C for about 30 minutes at a reduced pressure of 0.5 to 1.0 mm Hg with a nitrogen stream bleeding into the flask. The vacuum is removed and methyl benzoate (125 mL) is added dropwise and
30 stirring is continued at about 240°C for 5-10 minutes as the polymeric composition dissolves. The hot solution then is transferred to a 2-L beaker and stirring is continued as the solution cools. When the mixture becomes viscous, acetone (1 L) is added to facilitate
35 stirring. The crystalline polyester composition then is

- 34 -

collected by filtration, reslurried first in acetone (1 L) and then n-hexane (1 L) to remove the methyl benzoate and then dried in a vacuum oven under nitrogen. The polymer composition, consisting of poly(1,4-tetra-
5 methylene 2,6-naphthalenedicarboxylate) having copolymerized therein 9.75 weight percent of the residue of the compound of Example 1, is obtained in a yield of 207 g (91.6% of theory). The polymeric composition has an inherent viscosity of 0.135 measured in a 60/40 ratio
10 by weight phenol/tetrachloroethane mixture at a concentration of 0.5 g per 100 mL.

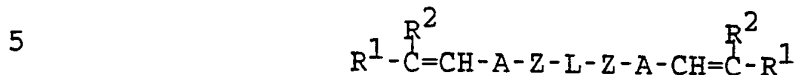
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and
15 modifications can be effected within the spirit and scope of the invention.

- 35 -

CLAIMS

We claim:

1. A compound having the formula



wherein

each R^1 is independently selected from cyano; carboxy; alkenyloxycarbonyl; an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical; an unsubstituted or substituted, carbocyclic or heterocyclic aryl radical; an unsubstituted or substituted alkanoyl, cycloalkanoyl or aroyl radical; an unsubstituted or substituted carbamoyl radical; or an unsubstituted or substituted alkylsulfonyl, cycloalkylsulfonyl or arylsulfonyl radical;

each R^2 is independently selected from cyano or an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical;

each A is independently selected from an unsubstituted or substituted 1,2-phenylene or 1,2-naphthylene radical;

each Z is independently selected from -O- or -S-; and

L is an organic linking group bonded by non-oxo carbon atoms to each Z atom.

2. A compound according to Claim 1 wherein each A is unsubstituted 1,2-phenylene.

3. A compound according to Claim 1 wherein

R^1 is an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical containing up to 24 carbon atoms;

- 36 -

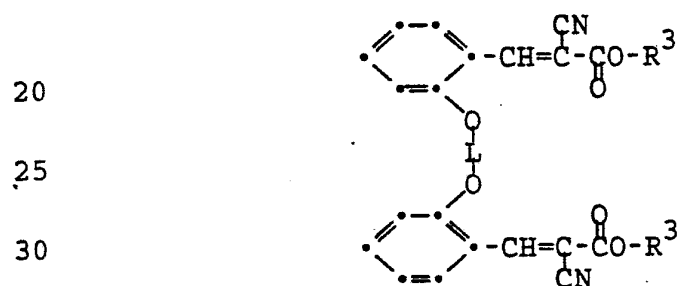
R^2 is cyano;

A is unsubstituted 1,2-phenylene;

Z is -O-; and

L is alkylene of up to 12 carbon atoms,
 5 2-hydroxy-1,3-propanediyl, 2-methyl-1,3-
 propanediyl, oxy-bis-ethylene, oxy-bis-1,4-
 butanediyl, sulfonyl-bis-ethylene, thio-bis-ethylene,
 1,2-, 1,3- and 1,4-phenylene-bis-methylene, 1,2-,
 1,3- and 1,4-phenylene-bis-ethylene, 1,4-
 10 cyclohexylene-bis-methylene, 1,2-, 1,3- and 1,4-
 phenylene-bis-(oxyethylene), methylsulfonylimino-bis-
 ethylene, phenylimino-bis-ethylene, acetylimino-bis-
 ethylene, phenylcarbamoylimino-bis-ethylene or 1,2-,
 1,3- and 1,4-phenylene.

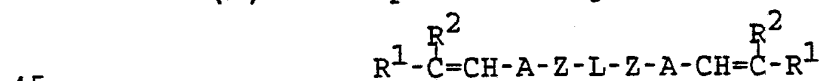
15 4. A compound having the formula



wherein R^3 is alkyl of up to 20 carbon atoms and
 L is alkylene of 2 to 8 carbon atoms, 1,2-, 1,3- or
 1,4-phenylenedimethylene or 1,2-, 1,3- or 1,4-
 phenylenediethylene.

40 5. A sunscreen composition comprising a solution,
 dispersion or suspension of

(1) a compound having the formula



wherein

each R^1 is independently selected from cyano;
 carboxy; alkenyloxycarbonyl; an unsubstituted or
 50 substituted alkoxy carbonyl, cycloalkoxy carbonyl or
 aryloxycarbonyl radical; an unsubstituted or

- 37 -

substituted, carbocyclic or heterocyclic aryl radical;
 an unsubstituted or substituted alkanoyl,
 cycloalkanoyl or aroyl radical; an unsubstituted or
 substituted carbamoyl radical; or an unsubstituted or
 5 substituted alkylsulfonyl, cycloalkylsulfonyl or
 arylsulfonyl radical;

each R^2 is independently selected from cyano
 or an unsubstituted or substituted alkoxy carbonyl,
 cycloalkoxy carbonyl or aryloxy carbonyl radical;

10 each A is independently selected from an
 unsubstituted or substituted 1,2-phenylene or
 1,2-naphthylene radical;

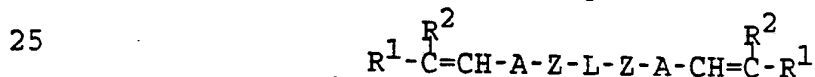
each Z is independently selected from -O- or
 -S-; and

15 L is an organic linking group bonded by non-
 oxo carbon atoms to each Z atom and

(2) a dermatologically-acceptable base.

6. A sunscreen composition according to Claim 5 in
 which A of the compound of component (1) is
 20 unsubstituted 1,2-phenylene.

7. A sunscreen composition according to Claim 5 com-
 prising a solution, dispersion or suspension of
 (1) a compound having the formula



wherein

R^1 is an unsubstituted or substituted
 alkoxy carbonyl, cycloalkoxy carbonyl or
 30 aryloxy carbonyl radical containing up to 24 carbon
 atoms;

R^2 is cyano;

A is unsubstituted 1,2-phenylene;

Z is -O-; and

35 L is alkylene of up to 12 carbon atoms,
 2-hydroxy-1,3-propanediyl, 2-methyl-1,3-

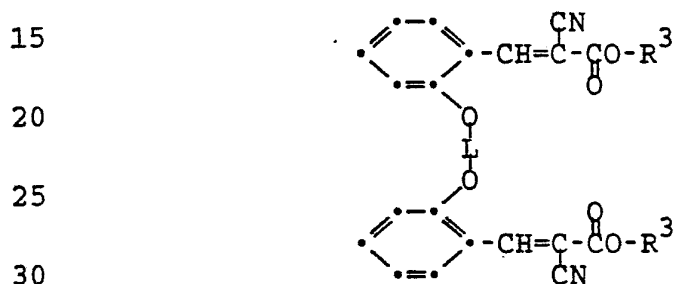
- 38 -

propanediyl, oxy-bis-ethylene, oxy-bis-1,4-butenediyl, sulfonyl-bis-ethylene, thio-bis-ethylene, 1,2-, 1,3- and 1,4-phenylene-bis-methylene, 1,2-, 1,3- and 1,4-phenylene-bis-ethylene, 1,4-

5 cyclohexylene-bis-methylene, 1,2-, 1,3- and 1,4-phenylene-bis-(oxyethylene), methylsulfonylimino-bis-ethylene, phenylimino-bis-ethylene, acetylimino-bis-ethylene, phenylcarbamoylimino-bis-ethylene or 1,2-, 1,3- and 1,4-phenylene; and

10 (2) a dermatologically-acceptable base.

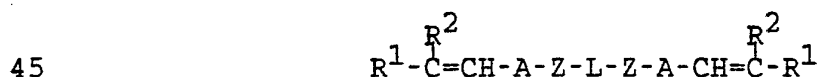
8. A sunscreen composition according to Claim 5 comprising a solution, dispersion or suspension of
- (1) a compound having the formula



wherein R^3 is alkyl of up to 20 carbon atoms and L is alkylene of 2 to 8 carbon atoms, 1,2-, 1,3- or 1,4-phenylenedimethylene or 1,2-, 1,3- or 1,4-phenylenediethylene; and

(2) a dermatologically-acceptable base.

9. A polymeric composition comprising a polyester having reacted therein or copolymerized therewith the residue of at least one poly-methine compound having the formula



wherein

each R^1 is independently selected from cyano; 50 carboxy; alkenyloxycarbonyl; an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or

- 39 -

aryloxycarbonyl radical; an unsubstituted or substituted, carbocyclic or heterocyclic aryl radical; an unsubstituted or substituted alkanoyl, cycloalkanoyl or aroyl radical; an unsubstituted or substituted carbamoyl radical; or an unsubstituted or substituted alkylsulfonyl, cycloalkylsulfonyl or arylsulfonyl radical;

each R^2 is independently selected from cyano or an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical;

each A is independently selected from an unsubstituted or substituted 1,2-phenylene or 1,2-naphthylene radical;

each Z is independently selected from -O- or -S-; and

L is an organic linking group bonded by non-oxo carbon atoms to each Z atom, provided the poly-methine compound bears at least one substituent that is reactive with one of the monomers from which the polyester is derived.

10. A polymeric composition comprising a polyester having reacted therein or copolymerized therewith 1.0 to 50.0 weight percent of the residue of at least one poly-methine compound defined in Claim 9 wherein

R^1 is an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical containing up to 20 carbon atoms;

R^2 is cyano;

A is unsubstituted 1,2-phenylene;

Z is -O-; and

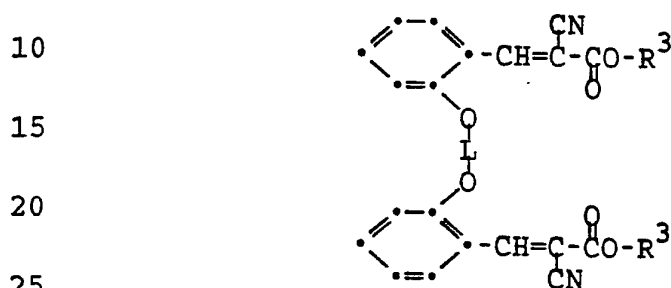
L is alkylene of up to 12 carbon atoms, 2-hydroxy-1,3-propanediyl, 2-methyl-1,3-propanediyl, oxy-bis-ethylene, oxy-bis-1,4-

- 40 -

- butanediyl, sulfonyl-bis-ethylene, thio-bis-ethylene, 1,2-, 1,3- and 1,4-phenylene-bis-methylene, 1,2-, 1,3- and 1,4-phenylene-bis-ethylene, 1,4-cyclohexylene-bis-methylene, 1,2-, 1,3- and 1,4-phenylene-bis-(oxyethylene), methylsulfonylimino-bis-ethylene, phenylimino-bis-ethylene, acetylimino-bis-ethylene, phenylcarbamoylimino-bis-ethylene or 1,2-, 1,3- and 1,4-phenylene.
- 5
11. A polymeric composition according to Claim 10
10 wherein the polyester has an inherent viscosity of 0.1 to 0.6 and is comprised of
- A. dicarboxylic acid residues comprised of at least 50 mole percent of terephthalic and/or 2,6-naphthalenedicarboxylic acid residues; and
- 15 B. diol residues comprised of at least 50 mole percent of ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol and/or 1,4-cyclohexanedimethanol residues.
12. A polymeric composition according to Claim 10
20 wherein the polyester has an inherent viscosity of 0.1 to 0.6 and is comprised of
- A. dicarboxylic acid residues comprised of at least 90 mole percent of terephthalic acid residues; and
- 25 B. diol residues comprised of at least 90 mole percent of ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol and/or 1,4-cyclohexanedimethanol residues.
13. A polymeric composition comprising a polyester
30 having an inherent viscosity of 0.1 to 0.6 comprised of
- A. dicarboxylic acid residues comprised of at least 90 mole percent of terephthalic acid residues; and

- 41 -

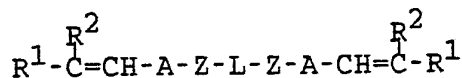
B. diol residues comprised of at least 90 mole percent of ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol and/or 1,4-cyclohexanedimethanol residues, having copolymerized therein 1.0 to 50.0 weight percent of a poly-methine compound having the formula



wherein R^3 is alkyl of up to 4 carbon atoms and L is alkylene of 2 to 8 carbon atoms, 1,2-, 1,3- or 1,4-phenylenedimethylene or 1,2-, 1,3- or 1,4-phenylenediethylene.

- 30
14. A sunscreen formulation comprising a solution, dispersion or suspension of
- (1) the polymeric composition of Claim 9; and
 - (2) a dermatologically-acceptable base.
- 35
15. A sunscreen formulation comprising a solution, dispersion or suspension of
- (1) the polymeric composition of Claim 11; and
 - (2) a dermatologically-acceptable base.
- 40
16. A sunscreen formulation comprising a solution, dispersion or suspension of (1) 0.1 to 20.0 weight percent, based on the weight of the formulation, of the polymeric composition of Claim 13; and (2) a dermatologically-acceptable base.
- 45
17. A polymeric composition comprising a casting, extrusion or molding grade condensation polymer having physically admixed therewith at least one poly-methine compound having the formula

- 42 -



5

wherein

each R^1 is independently selected from cyano; carboxy; alkenyloxycarbonyl; an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical; an unsubstituted or substituted, carbocyclic or heterocyclic aryl radical; an unsubstituted or substituted alkanoyl, cycloalkanoyl or aroyl radical; an unsubstituted or substituted carbamoyl radical; or an unsubstituted or substituted alkylsulfonyl, cycloalkylsulfonyl or arylsulfonyl radical;

10

15

each R^2 is independently selected from cyano or an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical;

20

each A is independently selected from an unsubstituted or substituted 1,2-phenylene or 1,2-naphthylene radical;

each Z is independently selected from -O- or -S-; and

25

L is an organic linking group bonded by non-oxo carbon atoms to each Z atom.

18. A polymeric composition comprising a casting, extrusion or molding grade polyester having physically admixed therewith 50 to 10,000 ppm of at least one poly-methine compound defined in Claim 17 wherein

30

R^1 is an unsubstituted or substituted alkoxy carbonyl, cycloalkoxy carbonyl or aryloxycarbonyl radical containing up to 20 carbon atoms;

35

R^2 is cyano;

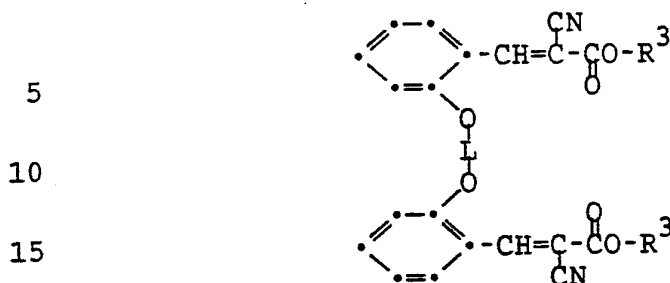
A is unsubstituted 1,2-phenylene;

Z is -O-; and

- 43 -

- L is alkylene of up to 12 carbon atoms, 2-hydroxy-1,3-propanediyl, 2-methyl-1,3-propanediyl, oxy-bis-ethylene, oxy-bis-1,4-butanediyl, sulfonyl-bis-ethylene, thio-bis-ethylene, 1,2-, 1,3- and 1,4-phenylene-bis-methylene, 1,2-, 1,3- and 1,4-phenylene-bis-ethylene, 1,4-cyclohexylene-bis-methylene, 1,2-, 1,3- and 1,4-phenylene-bis-(oxyethylene), methylsulfonylimino-bis-ethylene, phenylimino-bis-ethylene, acetylimino-bis-ethylene, phenylcarbamoylimino-bis-ethylene or 1,2-, 1,3- and 1,4-phenylene.
- 5
- 10
- 15
- 20
- 25
- 30
19. A polymeric composition according to Claim 18 wherein the polyester has an inherent viscosity of 0.4 to 1.2 and is comprised of
- A. dicarboxylic acid residues comprised of 75 to 100 mole percent terephthalic acid residues; and
- B. diol residues comprising 75 to 100 mole percent ethylene glycol residues.
20. A polymeric composition comprising a casting, extrusion or molding grade polyester having an inherent viscosity of 0.4 to 1.2 comprised of
- A. dicarboxylic acid residues comprised of 75 to 100 mole percent terephthalic acid residues; and
- B. diol residues comprising 75 to 100 mole percent ethylene glycol residues, having physically admixed therewith 50 to 1500 ppm of the residue of a poly-methine compound having the formula

- 44 -



20 wherein R^3 is alkyl of up to 4 carbon atoms and L is alkylene of 2 to 8 carbon atoms, 1,2-, 1,3- or 1,4-phenylenedimethylene or 1,2-, 1,3- or 1,4-phenylenediethylene.

21. A shaped article of the polymeric composition defined in Claim 17.
22. A film, sheet material or packaging material fabricated from the polymeric composition defined in Claim 18.
23. A film 25 to 254 microns thick extruded from the polymeric composition of Claim 18 wherein the concentration of the poly-methine compound is in the range of 1000 to 10,000.
24. A container fabricated from the polymeric composition of Claim 20.
25. A polymeric composition comprising a polyester having reacted therein or copolymerized therewith 50 to 10,000 ppm of the residue of at least one poly-methine compound defined in Claim 9 wherein R^1 is an unsubstituted or substituted alkoxy-carbonyl, cycloalkoxy-carbonyl or aryloxy-carbonyl radical containing up to 20 carbon atoms;
- R^2 is cyano;
- A is unsubstituted 1,2-phenylene;
- Z is -O-; and
- L is alkylene of up to 12 carbon atoms, 2-hydroxy-1,3-propanediyl, 2-methyl-1,3-propanediyl, oxy-bis-ethylene, oxy-bis-1,4-

butanediyl, sulfonyl-bis-ethylene, thio-bis-ethylene,
 1,2-, 1,3- and 1,4-phenylene-bis-methylene, 1,2-,
 1,3- and 1,4-phenylene-bis-ethylene, 1,4-
 cyclohexylene-bis-methylene, 1,2-, 1,3- and 1,4-
 5 phenylene-bis-(oxyethylene), methylsulfonylimino-bis-
 ethylene, phenylimino-bis-ethylene, acetylimino-bis-
 ethylene, phenylcarbamoylimino-bis-ethylene or 1,2-,
 1,3- and 1,4-phenylene.

26. A polymeric composition according to Claim 24
 10 wherein the polyester has an inherent viscosity of
 0.4 to 1.2 and is comprised of

A. dicarboxylic acid residues comprised of 75 to
 100 mole percent terephthalic acid residues;
 and

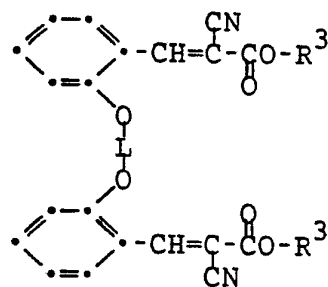
15 B. diol residues comprising 75 to 100 mole
 percent ethylene glycol residues.

27. A polymeric composition comprising a casting,
 extrusion or molding grade polyester having an
 inherent viscosity of 0.4 to 1.2 comprised of

20 A. dicarboxylic acid residues comprised of 75 to
 100 mole percent terephthalic acid residues;
 and

B. diol residues comprising 75 to 100 mole
 percent ethylene glycol residues,

25 having copolymerized therein 50 to 1500 ppm of
 the residue of a poly-methine compound having the
 formula



wherein R^3 is alkyl of up to 4 carbon atoms and
 L is alkylene of 2 to 8 carbon atoms, 1,2-, 1,3- or

- 46 -

1,4-phenylenedimethylene or 1,2-, 1,3- or 1,4-phenylenediethylene.

28. A shaped article of the polymeric composition defined in Claim 25.
- 5 29. A film, sheet material or packaging material fabricated from the polymeric composition defined in Claim 25.
30. A film 25 to 254 microns thick extruded from the polymeric composition of Claim 26 wherein the
10 concentration of the poly-methine compound is in the range of 1000 to 10,000.
31. A container fabricated from the polymeric composition of Claim 27.