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<p>(21) International Application Number: PCT/US89/03420 (22) International Filing Date: 10 August 1989 (10.08.89) (30) Priority data: 233,790 19 August 1988 (19.08.88) US (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventors: WEAVER, Max, Allen ; 125 Hill Road, Kingsport, TN 37664 (US). PRUETT, Wayne, Payton ; 101 Walton Court, Kingsport, TN 37663 (US). COATES, Clarence, Alvin, Jr. ; Rt. 13, Kingsport, TN 37664 (US). HILBERT, Samuel, David ; Rt. 7, Jonseborough, TN 37659 (US). (74) Agent: THOMSEN, J., Frederick; 343 State Street, Rochester, NY 14650 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i></p>
<p>(54) Title: CONDENSATION POLYMERS CONTAINING METHINE ULTRAVIOLET RADIATION-ABSORBING RESIDUES AND SHAPED ARTICLES PRODUCED THEREFROM</p>		
$R^1-S-A-CH=C \begin{matrix} O \\ \\ R^3 \end{matrix} CO-R^2 \quad (I)$ $-C(=O)OR^2 \quad (\alpha)$		
<p>(57) Abstract</p> <p>A composition useful for molding into articles such as food containers, soft drink bottles, cured structural plastics and the like, comprising molding grade linear or unsaturated polyester or polycarbonate having reacted or copolymerized therein the residue of one or a mixture of methine reactants of formula (I), wherein R¹ is an unsubstituted or substituted alkyl, cycloalkyl or aryl radical; A is an unsubstituted or substituted 1,4-phenylene radical; R² is hydrogen or an unsubstituted or substituted alkyl, alkenyl, cycloalkyl or aryl radical; R³ is cyano, α or an unsubstituted or substituted carbamoyl, alkanoyl, aroyl, alkylsulfonyl, arylsulfonyl, aryl or aromatic heterocyclic radicals. The methine residues are present in the polymer as an integral part of the polymer chain and absorb ultraviolet radiation in the range of 250 to 390 nm. The residues are non-extractable from the polymer and stable at the conditions at which the polymers are manufactured and processed.</p>		

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DescriptionCondensation Polymers Containing Methine
Ultraviolet Radiation-Absorbing Residues
and Shaped Articles Produced Therefrom

5 This invention pertains to novel condensation
polymers such as polyesters and polycarbonates wherein
an ultraviolet light screening amount of one or more
methine moieties has been incorporated in the chain or
backbone of the polymer. This invention also pertains
10 to containers, such as those suitable for packaging
beverages and foods, manufactured from our novel
condensation polymers.

 Many products such as certain fruit juices, soft
drinks, wines, food products, cosmetics and shampoos
15 are deleteriously affected, i.e., degraded, by ultra-
violet (UV) light when packaged in plastic containers
which pass significant portions of the available light
at wavelengths in the range of approximately 250 to
390 nm. It is well known that polymers can be rendered
20 resistant to degradation by UV light by physically
blending in such polymers various UV light stabilizers
such as benzophenones, benzotriazoles and resorcinol
monobenzoates. See, for example, *Plastics Additives
Handbook*, Hanser Publishers, Library of Congress,
25 Catalog No. 83-062289, pp 128-134. Normally, such
stabilizers are used in a weight concentration of at
least 0.5 percent. Although these stabilizers function
well to absorb radiation in the range of 300 to 350 nm,
absorbance in the range of 300 to 350 nm is not adequate
30 to protect comestibles subject to UV light degradation
packaged in clear plastic, i.e., essentially colorless,
transparent plastic. The stabilizers in the known
stabilized polymer compositions can be extracted from
the polymer by solvents such as acids, alcohols and the

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like present in foods or beverages packaged within the stabilized polymers. Furthermore, many compounds used to stabilize polymers are not stable at high temperatures and would decompose under the conditions at which

5 polyesters are manufactured or processed. Decomposition of such stabilizers frequently causes yellow discoloration of the polyester and results in the polyester containing little, if any, of the stabilizer.

U.S. Patent 4,340,718 discloses the copolymerization

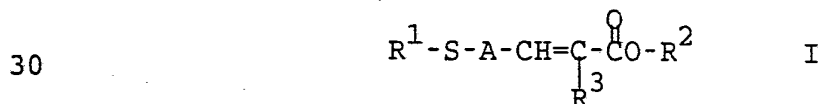
10 of certain methine stabilizers with polyesters. The patent further discloses that the concentration of the methine stabilizers in the polyesters should be in the range of 0.3 to 5.0 percent, preferably 0.6 to 2.0 percent, i.e., 6000 to 20,000 ppm, to impart to the

15 basic polyester improved weatherability in outdoor applications. This patent does not mention the use of methine compounds in low concentrations for the purpose of screening UV light.

U.S. Patent 4,617,374 discloses polyesters having

20 certain methine compounds reacted therein to absorb light in the range of 320 to 380 nm. That patent, however, does not disclose the methine compounds used in the polyester compositions and articles molded therefrom provided by our invention.

25 Our invention concerns a composition comprising molding grade condensation polymer having copolymerized therein the residue of a methine compound or mixture of methine compounds having the formula



wherein

R^1 is an unsubstituted or substituted alkyl, cycloalkyl or aryl radical;

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A is an unsubstituted or substituted 1,4-phenylene radical;

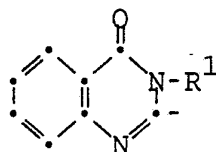
R^2 is hydrogen or an unsubstituted or substituted alkyl, alkenyl, cycloalkyl or aryl radical; and

5 R^3 is $\overset{\text{O}}{\parallel}\text{CO-R}^2$, cyano or an unsubstituted or substituted carbamoyl, alkanoyl, aroyl, alkylsulfonyl, arylsulfonyl, aryl or aromatic heterocyclic radicals.

R^3 preferably is $\overset{\text{O}}{\parallel}\text{CO-R}^2$ or cyano.

10 Examples of the unsubstituted alkyl groups include methyl, ethyl, propyl, 2-propyl, butyl, 2-butyl, hexyl, octyl, 2-ethylhexyl, decyl, dodecyl, etc. The cycloalkyl groups may be cyclopentyl, cyclohexyl, cycloheptyl and the like. The aryl groups may be, for example,
 15 carbocyclic aryl such as phenyl and naphthyl. Examples of the unsubstituted alkanoyl, alkylsulfonyl and arylsulfonyl include acetyl, propionyl, butyryl, pivaloyl, hexanoyl, 2-ethylhexanoyl, methylsulfonyl, ethylsulfonyl, propylsulfonyl, octylsulfonyl, phenylsulfonyl, etc.
 20 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

25



are examples of the unsubstituted aromatic heterocyclic residues which may constitute a part of the methine
 30 compounds. The alkyl radicals represented by R^1 and R^2 can be substituted with a wide variety of substituents such as alkoxy, alkylthio, halogen, hydroxy, cycloalkyl, cycloalkoxy, alkanoyloxy, cyano, aryl, aryloxy, arylthio, etc. The cycloalkyl, aryl and aromatic heterocyclic

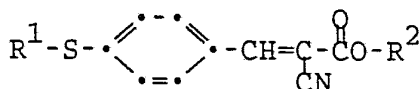
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groups can be substituted with unsubstituted or substituted alkyl as well as with any of the substituents set forth hereinabove. Normally, those substituents containing alkyl moieties, such as alkyl, hydroxyalkyl, alkoxyalkyl, etc., will not contain more than a total of 12 carbon atoms. The unsubstituted and substituted cycloalkyl groups typically will contain from 5 to 12 carbon atoms whereas the unsubstituted and substituted aryl groups will contain from 6 to 12 carbon atoms. Illustrative of the 1,4-phenylene radical represented by A is the group having the structure



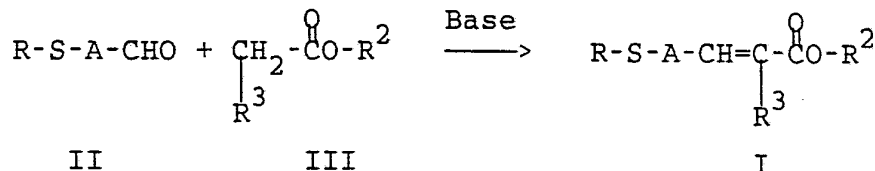
wherein R^4 is hydrogen, alkyl, alkoxy or halogen.

The methine compounds which are particularly preferred have the formula



wherein R^1 and R^2 are lower alkyl, in which lower designates a carbon content of up to 4 carbon atoms.

The methine compounds may be prepared using known procedures by reacting an intermediate aldehyde compound II with an active methylene compound III under Knoevenagel reaction conditions, e.g.,



Lower alcohols such as methanol, ethanol and 2-propanol are usually suitable solvents. With certain reactants, for example when R^3 is

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$\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-R}^2$, it is sometimes advantageous to conduct the reaction in a hydrocarbon solvent such as benzene or toluene to permit the water of reaction to be azeotropically removed as it is formed. Bases such as
5 piperidine, piperidine acetate, pyrrolidine, sodium acetate and pyridine are effective in promoting the reaction.

The polyesters which may be used in the preparation of the compositions of our invention include
10 linear, thermoplastic, crystalline or amorphous polyesters produced by conventional polymerization techniques from one or more diols and one or more dicarboxylic acids. The polyesters normally are molding or fiber grade and have an inherent viscosity (IV) of
15 0.4 to 1.2. The preferred polyesters comprise at least 50 mole percent terephthalic acid residues and at least 50 mole percent ethylene glycol and/or 1,4-cyclohexanedimethanol residues. Particularly preferred polyesters are those containing from 75 to 100 mole percent
20 terephthalic acid residues and from 75 to 100 mole percent ethylene glycol residues.

The unsaturated, curable polyesters which may be used in our novel compositions are the polyesterification products of one or more glycols and one or more
25 unsaturated dicarboxylic acids or their anhydrides. Typical of the unsaturated polyesters is the polyesterification product of (a) 1,4-cyclohexanedimethanol and/or 2,2-dimethyl-1,3-propanediol and optionally an additional dihydric alcohol, such as
30 ethylene glycol, and (b) maleic acid or fumaric acid and an aromatic dicarboxylic acid, which when crosslinked with an ethylenically-unsaturated monomer, e.g., styrene, produces a cured polyester resin which has, for example, high thermal resistance, high heat distortion values,

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excellent electrical and mechanical properties, and excellent resistance to chemicals.

Solutions of such unsaturated polyester resins in an ethylenically-unsaturated monomer such as styrene
5 commonly are referred to as polyester resins.

The unsaturated polyester resins may be prepared in the presence of gelation inhibitors such as hydroquinone or the like, which are well known in the art of polyesterification. The esterification may be carried
10 out for example under an inert blanket of gas such as nitrogen in a temperature range of 118°-220°C for a period of 6-20 hours until an acid number below 100 and preferably below 50 is obtained, based on milliequivalents
15 of KOH necessary to neutralize 1 gram of the unsaturated polyester. The resulting polyester may be subsequently copolymerized, crosslinked, or cured with "curing amounts" of any of the well-known ethylenically
unsaturated monomers used as solvents for the polyester. Examples of such monomers include styrene, alpha-methyl
20 styrene, vinyl toluene, divinyl benzene, chlorostyrene, and the like as well as mixtures thereof. Typically, the mole ratio of such unsaturated monomer to the unsaturated moiety (e.g., maleic acid residue) in the polyester is from 0.5 to 3.0, although the "curing
25 amounts" of such monomer can be varied from these ratios.

It is preferred that the unsaturated polyester be prepared from one or more dihydric alcohols, fumaric or maleic acid or mixtures thereof, and up to 60 mole percent of total acid component of o-phthalic, iso-
30 phthalic or terephthalic acids or mixtures thereof. Preferred for the dihydric alcohol component is one or a mixture of propylene glycol, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol, ethylene glycol, or diethylene glycol. A specific preferred unsaturated
35 polyester is prepared from 75 to 100 mole percent

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propylene glycol, and as the acid component, from 75 to 100 mole percent o-phthalic and maleic acids in a mole ratio of from 1/2 to 2/1. Typical of these unsaturated polyesters are those disclosed, for example, in U.S.

5 Patent 4,359,570 incorporated herein by reference.

The diol components of the described linear polyesters may be selected from ethylene glycol, 1,4-cyclohexanedimethanol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 10 1,6-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, X,8-bis(hydroxymethyl)tricyclo-[5.2.1.0]-decane wherein X represents 3, 4, or 5; and diols containing one or more oxygen atoms in the chain, e.g., diethylene glycol, 15 triethylene glycol, dipropylene glycol, tripropylene glycol and the like. In general, these diols contain 2 to 18, preferably 2 to 8 carbon atoms. Cycloaliphatic diols can be employed in their cis or trans configuration or as mixtures of both forms.

20 The acid components (aliphatic, alicyclic, or aromatic dicarboxylic acids) of the linear polyester are selected, for example, from terephthalic acid, isophthalic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, succinic acid, glutaric 25 acid, adipic acid, sebacic acid, 1,12-dodecanedioic acid, 2,6-naphthalene-dicarboxylic acid and the like. In the polymer preparation, it is often preferable to use a functional acid derivative thereof such as the dimethyl, diethyl, or dipropyl ester of the dicarboxylic acid. 30 The anhydrides or acid halides of these acids also may be employed where practical.

Typical polycarbonates useful herein are disclosed in Kirk-Othmer Encyclopedia of Chemical Technology, third edition, Volume 18, pages 479-494, incorporated 35 herein by reference.

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The polyester compositions provided by this invention may be prepared by reacting under polyester-forming conditions of temperature and pressure at least one of the dicarboxylic acids, or an ester forming equivalent, and at least one of the diols described above in the presence of at least one of the methine compounds of Formula I. For example, approximately equimolar amounts of one or more dicarboxylic acids and one or more diols may be reacted in the presence of a conventional polyesterification catalyst for a period of time sufficient to obtain a polyester having the desired inherent viscosity, e.g., an inherent viscosity of 0.4 to 1.2. The methine compound may be included initially with the diol and dicarboxylic acid reactants or it may be added during the polycondensation reaction.

Typically, the polyester composition is prepared at temperatures in the range of 200 to 300°C and pressures in the range of 50 psig (444.7 kPa) to 4.0 mm Hg (0.53 kPa). The initial esterification or transesterification reaction may be conducted at a temperature of 200 to 230°C and at ambient pressure or a pressure moderately above ambient pressure. As the polycondensation reaction proceeds, the temperature is increased and the pressure is decreased. For example, at the completion of the polycondensation reaction, the temperature may be in the range of 280 to 300°C and the pressure may be as low as 4.0 mm Hg (0.53 kPa).

The novel polymer compositions provided by this invention are useful in the manufacture of containers or packages for comestibles such as beverages and food. By the use of known heat-setting techniques, certain of the polyesters are, in terms of color, I.V. and heat distortion, stable at temperatures up to 100°C. Such stability characteristics are referred to herein as "hot-fill" stability. Articles molded from these

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polyesters exhibit good thin-wall rigidity, excellent clarity and good barrier properties with respect to moisture and atmospheric gases, particularly carbon dioxide and oxygen.

5 The linear polyesters most preferred for use in articles having "hot-fill" stability comprise poly(ethylene terephthalate) and poly(ethylene terephthalate) wherein up to 5 mole percent of the ethylene glycol residues have been replaced with residues
10 derived from 1,4-cyclohexanedimethanol, wherein the polyesters have been sufficiently heat set and oriented by methods well known in the art to give a desired degree of crystallinity. By definition, a polymer is "hot-fill" stable at a prescribed temperature when less
15 than 2% change in volume of a container manufactured therefrom occurs upon filling the same with a liquid at the temperature. For the manufacture of blow-molded beverage bottles, the most preferred polyesters have an I.V. of 0.65 to 0.85 and a Tg of >70°C. The Tg is
20 determined by Differential Scanning Calorimetry at a scan rate of 20 Centigrade Degrees/min., the Oxygen Permeability by the standard operating procedure of a MOCON OXTRAN 100 instrument of Modern Controls, Inc., of Elk River, Minnesota, and the Carbon Dioxide Permeability
25 by the standard operating procedure of a MOCON PERMATRAN C II, also of Modern Controls.

 The concentration of the residue of the methine compound in the condensation polymer can be varied substantially depending, for example, on the intended
30 function of the UV-absorbing residue and/or the end use for which the polymer composition is intended. When the polymer composition is to be used in the fabrication of relatively thin-walled containers to screen UV light in the range of 250 to 390 nm, the concentration of the
35 residue of the methine compound normally will be in the

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range of 50 to 1,500 ppm (parts by weight per million parts by weight polymer) with the range of 200 to 800 ppm being especially preferred.

When the levels of the present ultraviolet light absorbers are increased to higher levels such as 5,000 ppm (0.5 weight percent) or higher, polymers containing these ultraviolet light absorbers show improved resistance to weathering and when these polymers per se or fibers thereof are dyed with disperse dyes, at a concentration, for example, of from 0.01% to 5.0% based on weight of polymer or fiber, many dyes exhibit increased lightfastness. Such disperse dyes are shown, for example, in U.S. Patents: 4,305,719; 2,746,952; 2,746,953; 2,757,173; 2,763,668; 2,771,466; 2,773,054; 2,777,863; 2,785,157; 2,790,791; 2,798,081; 2,805,218; 2,822,359; 2,827,450; 2,832,761; 2,852,504; 2,857,371; 2,865,909; 2,871,231; 3,072,683; 3,079,373; 3,079,375; 3,087,773; 3,096,318; 3,096,332; 3,236,843; 3,254,073; 3,349,075; 3,380,990; 3,386,990; 3,394,144; 3,804,823; 3,816,388; 3,816,392; 3,829,410; 3,917,604; 3,928,311; 3,980,626; 3,998,801; 4,039,522; 4,052,379; and 4,140,683, the disclosures of which are incorporated herein by reference.

Polymer compositions containing substantially higher amounts, e.g., from 2.0 to 10.0 weight percent, of the residue of one or more of the methine compounds described herein may be used as polymer concentrates. Such concentrates may be blended with the same or different polymer according to conventional procedures to obtain polymer compositions which will contain a predetermined amount of the residue or residues in a nonextractable form. In the preparation of these highly loaded, polymer composition concentrates the residue preferably is divalent and thus is derived from a difunctional methine compound such as the compounds

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wherein R¹ is hydroxyalkyl and/or R³ is $-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2$.

The preparation of the methine compounds and their use in preparing the compositions of our invention are further illustrated by the following examples.

5

Example 1

4-(Methylthio)benzaldehyde (1.52 g., .01 mol), methyl cyanoacetate (1.0 g, .01 mol), methanol (15 mL), and piperidine (5 drops) are mixed and heated at reflux
10 for 1 hour. Upon cooling, the pale yellow solid crystallizes and is collected by filtration, washed with methanol and dried in air. The yield is 2.3 g, 98.7% of the theoretical yield, of methyl 2-cyano-3-[4-(methylthio)phenyl]-2-propenoate. When dissolved in
15 methylene chloride, the compound has an absorption maximum (λ_{max}) at 365 nm in the ultraviolet absorption. The structure of the product is confirmed by mass spectroscopy analysis.

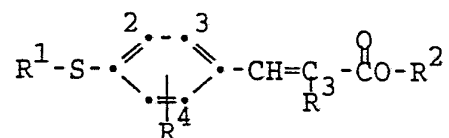
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Example 2

4-(Methylthio)benzaldehyde (3.04 g, .02 mol), diethyl malonate (3.20 g, .02 mol), toluene (25 mL), piperidine (4 drops) and acetic acid (2 drops) are mixed and heated at reflux for 2 hours with the water
25 formed being removed azeotropically. The solution is cooled and 25 mL of water added with stirring. After separation of the layers, the toluene is evaporated from the organic layer to yield the product, diethyl 2-[[4-(methylthio)phenyl]methylene]propanedioate, in
30 essentially quantitative yield. When dissolved in methylene chloride, the product has an absorption maximum (λ_{max}) at 330 nm in the ultraviolet absorption spectrum. The identity of the product is confirmed by mass spectroscopy analysis.

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Additional examples of methine compounds which may be used in the preparation of our novel polymer compositions are set forth in the following table. These compounds may be prepared according to the procedures described above and conform to the formula



TABLE

Ex.	R ¹	R ²	R ³	R ⁴
3	-CH ₃	-C ₂ H ₅	-CN	H
4	-C ₂ H ₅	-CH ₃	-CN	H
5	-C ₆ H ₅	-CH ₃	-CN	H
6	-C ₆ H ₁₁	-CH ₃	-CN	H
7	-CH ₂ C ₆ H ₅	-C ₂ H ₅	-CN	H
8	-C ₆ H ₄ -4-CH ₃	-CH(CH ₃) ₂	-CN	3-CH ₃
9	-C ₆ H ₄ -4-Cl	-(CH ₂) ₃ H	-CN	2-CH ₃
10	-C ₆ H ₄ -3-OCH ₃	-CH ₃	-COOCH ₃	2,6-di-CH ₃
11	-CH ₂ C ₆ H ₄ -4-CH ₃	-C ₂ H ₅	-COOC ₂ H ₅	3-CH ₃
12	-CH ₂ CH ₂ C ₆ H ₅	-CH ₃	-COOCH ₃	3-OCH ₃
13	-C ₆ H ₁₀ -4-CH ₃	-CH ₃	-COOCH ₃	-2-CH ₃ -5-OCH ₃
14	-CH ₃	-CH ₂ CH ₂ OH	-CN	H
15	-CH ₃	-CH ₂ CH ₂ OCH ₃	-CN	H
16	-CH ₃	-CH ₂ CH ₂ CN	-CN	H
17	-CH ₃	-CH ₂ CH ₂ OOCCH ₃	-CN	H
18	-CH ₃	-CH ₂ C ₆ H ₅	-CN	H
19	-(CH ₂) ₄ H	-CH ₂ CH ₂ OC ₆ H ₅	-CN	H

TABLE (Continued)

Ex.	R ¹	R ²	R ³	R ⁴
20	-CH ₂ CH(CH ₃) ₂	-CH ₂ C ₆ H ₁₀ -4-CH ₂ OH	-CN	H
21	-CH ₃	-CH ₂ C ₆ H ₁₁	-CN	H
22	-CH ₃	-CH ₂ CH ₂ Cl	-CN	H
23	-CH ₃	-CH ₂ CH ₂ NHCOCH ₃	-CN	H
24	-CH ₃	-(CH ₂ CH ₂ O) ₂ H	-CN	H
25	-CH ₃	-CH ₂ CH(OH)CH ₂ OH	-CN	H
26	-CH ₃	-C ₆ H ₅	-CN	H
27	-CH ₃	-CH ₂ C=CHCH=CHO	-CN	H
28	-CH ₃	-CH ₂ CHCH ₂ CH ₂ CH ₂ O	-CN	H
29	-CH ₃	-CH ₂ CH ₂ C ₆ H ₅	-CN	H
30	-CH ₃	-(CH ₂ CH ₂ O) ₂ C ₂ H ₅	-CN	H
31	-CH ₃	-CH ₂ C ₆ H ₁₀ -4-CH ₂ OOCCH ₃	-CN	H
32	-CH ₃	-CH ₂ -CH ₂ SCH ₂ CH ₂ OH	-CN	H
33	-CH ₃	-(CH ₂) ₄ H	-COO(CH ₂) ₄ H	H
34	-C ₂ H ₅	H	-SO ₂ CH ₃	H
35	-C ₂ H ₅	-CH ₃	-CONH ₂	H

TABLE (Continued)

Ex.	R ¹	R ²	R ³	R ⁴
36	-(CH ₂) ₄ H	-CH ₃	-CONHCH ₂ CH ₂ OH	H
37	-CH ₃	-CH ₃	-SO ₂ C ₆ H ₅	H
38	-CH ₃	-CH ₃	-C=N-1,2-C ₆ H ₄ O	H
39	-CH ₃	-C ₂ H ₅	-C=N-1,2-C ₆ H ₄ S	H
40	-CH ₃	-C ₂ H ₅	-C ₆ H ₄ -4-CN	H
41	-CH ₃	-C ₂ H ₅	-C ₆ H ₄ -4-COOCH ₃	H
42	-C ₂ H ₅	-C ₂ H ₅	-CONHC ₆ H ₅	H
43	-C ₂ H ₅	-CH ₃	-CON(C ₂ H ₅) ₂	H
44	-C ₂ H ₅	-CH ₃	-CON(CH ₃)C ₆ H ₅	H
45	-C ₂ H ₅	-CH ₃	-C=CHCH=C(COOCH ₃) ₂ S	H
46	-C ₂ H ₅	-CH ₃	-C=NN=C(CH ₃) ₂ S	H
47	-CH ₃	-CH ₃	-C=N-1,2-C ₆ H ₄ NH	H
48	-CH ₃	-CH ₃	-C=NN=C(CH ₃) ₂ O	H
49	-CH ₃	-CH ₃	-SO ₂ C ₆ H ₁₁	H
50	-CH ₃	H	-COOH	H

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EXAMPLE 51

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

- 97 g (0.5 mol) dimethyl terephthalate
- 5 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 of manganese acetate
- 10 0.0345 g antimony trioxide
- 0.0072 g Co from an ethylene glycol solution of cobaltous acetate

The flask is equipped with a nitrogen inlet, stirrer, 15 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 of an ethylene glycol slurry of a mixed phosphorus 20 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, methyl 2-cyano-3-[4-(methylthio)phenyl]-2-propenoate (0.0384 g) is added to the flask. Five minutes after this addition, a vacuum 25 with a slow stream of nitrogen bleeding in the system is applied over a five-minute period until the pressure is reduced to 200 mm Hg (26.7 kPa). The flask and contents are heated at 230°C under a pressure of 200 mm Hg (26.7 kPa) for 25 minutes. The metal bath temperature is 30 increased to 270°C. At 270°C the pressure is reduced slowly to 100 mm Hg (13.3 kPa). The flask and contents are heated at 270°C under a pressure of 100 mm Hg (13.3 kPa) for 30 minutes. The metal bath temperature is increased to 285°C and the pressure is reduced slowly to 35 4.5 mm Hg (0.6 kPa). The flask and contents are heated

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at 285°C under pressure of 4.5 mm Hg (0.6 kPa) for 25 minutes. Then the pressure is reduced to 0.25 mm Hg (0.03 kPa) and polycondensation is continued for 40 minutes. The flask is removed from the metal bath and
5 is allowed to cool in a nitrogen atmosphere while the polymer crystallizes. The resulting polymer has an inherent viscosity of 0.58 measured in a 60/40 ratio by weight of phenol/tetrachloroethane at a concentration of 0.5 g per 100 mL. An amorphous film molded from this
10 polymer to simulate the sidewall of a container showed a strong absorption at 380 nm.

Example 52

The procedure described in Example 51 is repeated
15 using 0.0384 g diethyl 2-[[4-(methylthio)phenyl]-methylene]propanedioate obtained in Example 2 instead of the methine compound used in Example 51. The resulting polymer has an inherent viscosity of 0.56 measured in a 60/40 ratio by weight of phenol/tetrachloroethane at a
20 concentration of 0.5 g per 100 mL. An amorphous film molded from this polymer shows a strong absorption peak with a maximum at 342 nm.

The inherent viscosities (I.V. of the copolyesters described herein are determined according to ASTM
25 D2857-70 procedure in a Wagner Viscometer of Lab Glass Inc. of Vineland, N.J. having a 1/2 ml capillary bulb, using a polymer concentration of 0.5%, by weight, in 60/40, by weight, phenol/tetrachloroethane solvent. The procedure comprises heating the polymer/solvent
30 system at 120°C for 15 minutes to enhance dissolution of the polymer, cooling the solution to 25°C and measuring the time of flow at 25°C. The I.V. is calculated from the equation

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2. 50% Ethanol/Water. The samples at room temperature are added to the solvent at room temperature, placed in an oven at 49°C and analyzed after 24 hours and again after 30 days.

5 3. Heptane. The samples at room temperature are added to solvent at room temperature and heated at 65.5°C for two hours. Part of the samples are cooled to room temperature and analyzed spectrophotometrically and the remainder are allowed to age at 49°C for 30
10 days before analysis.

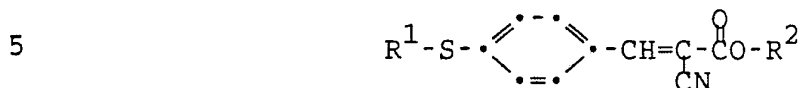
Any suitable analytical technique and apparatus may be employed to determine the amount of methine residue extracted from the polymer.

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

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3. A composition of Claim 1 wherein the polymer is a linear polyester and the methine compound has the formula



wherein

R^1 and R^2 are lower alkyl.

- 10 4. The composition of Claim 2 wherein the polyester acid moiety is comprised of at least 50 mol % terephthalic acid residue, and the glycol moiety at least 50 mol % ethylene glycol or 1,4-cyclohexanedimethanol residue.
- 15 5. The composition of Claim 3 wherein the polyester is comprised of from 75 to 100 mol % terephthalic acid residue and from 75 to 100 mol % ethylene glycol residue.
- 20 6. The composition of Claim 1 wherein the polymer is unsaturated polyester having an acid moiety comprised of fumaric or maleic acid or mixtures thereof and up to 60 mol % of one or a mixture of
- 25 o-phthalic, isophthalic, or terephthalic acids, and having a glycol moiety comprised of one or a mixture of propylene glycol, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol, ethylene glycol or diethylene glycol.
- 30 7. The composition of Claim 6 wherein the acid moiety is comprised of from 75 to 100 mol % o-phthalic acid and maleic acid in a mole ratio of from 1/2 to

2/1, and the glycol moiety is comprised of from 75 to 100 mol % propylene glycol.

8. A fiber of the composition of Claim 2 dyed with
5 from 0.01 to 5.0% by weight based on weight of fiber of a disperse dye.
9. A formed article of the composition of Claim 2.
10. A formed article of the composition of Claim 4.
11. A container formed of the composition of Claim 5.
12. A method for preparing a molding grade polyester
15 composition by the reaction of at least one dicarboxylic acid, or an ester-forming equivalent thereof, and at least one diol at temperatures of 200 to 300°C and pressures of 444.7 to 0.53 kPa until a polyester having an inherent viscosity of
20 0.4 to 1.2 is obtained, characterized in that said reaction is carried out in the presence of a methine compound or mixture of methine compounds having the formula



wherein

R^1 is an unsubstituted or substituted alkyl, cycloalkyl or aryl radical;

30 A is an unsubstituted or substituted 1,4-phenylene radical;

R^2 is hydrogen or an unsubstituted or substituted alkyl, alkenyl, cycloalkyl or aryl radical; and

35 R^3 is $-\overset{O}{\parallel}CO-R^2$, cyano or an unsubstituted or

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/03420

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶				
According to International Patent Classification (IPC) or to both National Classification and IPC				
IPC ⁵ : C 08 G 63/688, //C 07 C 323/62, C 07 C 323/32				
II. FIELDS SEARCHED				
Minimum Documentation Searched ⁷				
Classification System	Classification Symbols			
IPC ⁵	C 08 G			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸				
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹				
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³		
P, X	US, A, 4845188 (M.A. WEAVER et al.) 4 July 1989, see the whole document --	1-14		
A	US, A, 4749772 (M.A. WEAVER et al.) 7 June 1988, see claims 1,4,5,8-11, 14-19; column 1, lines 10-25; column 2, lines 55-65 --	1,4-8,11		
A	US, A, 4340718 (J.S. ZANNUCCI et al.) 20 July 1982, see claims 1,2 cited in the application --	1		
A	WO, A, 86/04903 (EASTMAN KODAK CO.) 28 August 1986, see claims 1,2,7,10 cited in the application ----	1,4,9,10		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> ⁹ Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family </td> </tr> </table>			⁹ Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family
⁹ Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family			
IV. CERTIFICATION				
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report			
14th November 1989	18. 12. 89			
International Searching Authority	Signature of Authorized Officer			
EUROPEAN PATENT OFFICE	T.K. WILLIS			

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8903420
SA 31093

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 12/12/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4845188	04-07-89	None	
US-A- 4749772	07-06-88	None	
US-A- 4340718	20-07-82	None	
WO-A- 8604903	28-08-86	US-A- 4617374	14-10-86
		AU-B- 579923	15-12-88
		AU-A- 5513686	10-09-86
		AU-B- 579233	17-11-88
		AU-A- 5544986	10-09-86
		CA-A- 1261532	26-09-89
		EP-A- 0217823	15-04-87
		EP-A- 0215054	25-03-87
		JP-T- 62501856	23-07-87
		JP-T- 62501857	23-07-87
		WO-A- 8604904	28-08-86
		US-A- 4617373	14-10-86

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