



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification³ : C08L 61/28, 75/06	A1	(11) International Publication Number: WO 85/ 01737 (43) International Publication Date: 25 April 1985 (25.04.85)
(21) International Application Number: PCT/US83/01604 (22) International Filing Date: 13 October 1983 (13.10.83) (71) Applicant (for AU only): FORD MOTOR COMPANY OF CANADA, LIMITED [CA/CA]; The Canadian Road, P.O. Box 200, Oakville, Ontario L6J 5EA (CA). (71) Applicant (for AU JP only): FORD MOTOR COMPANY [US/US]; The American Road, Dearborn, MI 48121 (US). (72) Inventors; and (75) Inventors/Applicants (for US only) : KORDOMENOS, Panagiotis, I. [GR/US]; 42758 Elizabeth Circle, Mt. Clemens, MI 48044 (US). KURPLE, Kenneth, R. [US/US]; 9533 Springborn Road, Anchorville, MI 48004 (US). ALEXANDER, Delores, J. [US/US]; 29060 Lone Elm Lane, Southfield, MI 48076 (US).		(74) Agents: MELOTIK, Lorraine, S. et al.; Office of the General Counsel, Ford Motor Company, Suite 911, Parklane Towers East, One Parklane Blvd., Dearborn, MI 48126 (US). (81) Designated States: AU, JP, US. Published <i>With international search report.</i>
(54) Title: FLEXIBLE UNI-BASECOAT/TWO COMPONENT CLEARCOAT COATING COMPOSITIONS (57) Abstract Flexible basecoat/clearcoat coating systems which have excellent adherence to metal and plastic substrates and possess superior weathering properties. The clearcoat composition comprises hydroxy-containing urethane modified polyester, made by reacting a urethane modified diol with polyol and diacid component, and crosslinking agent. The crosslinking agent of the pigmented basecoat composition comprises amine-aldehyde crosslinking agent. The crosslinking agent of the clearcoat comprises polyisocyanate crosslinking agent. Optionally, either or both compositions may comprise a high molecular weight linear polyurethane.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GA	Gabon	MR	Mauritania
AU	Australia	GB	United Kingdom	MW	Malawi
BB	Barbados	HU	Hungary	NL	Netherlands
BE	Belgium	IT	Italy	NO	Norway
BG	Bulgaria	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali		
FR	France				

- 1 -

FLEXIBLE UNI-BASECOAT/TWO COMPONENT CLEARCOAT
COATING COMPOSITIONS

This invention relates to flexible coating systems which have excellent adherence to metal and plastic substrates and possess superior weathering properties. Basecoat/clearcoat systems comprise a finish of a clear topcoat layer in film adherence to a basecoat that is in adherence to a substrate. More particularly, the invention relates to a basecoat/clearcoat coating composition wherein the basecoat and the clearcoat composition each comprise hydroxy-containing urethane modified polyesters, made from urethane modified diols reacted with polyol and diacid component, crosslinking agent and, optionally, a high molecular weight linear polyurethane. The basecoat, which additionally contains pigment, employs amine-aldehyde crosslinking agent while the clearcoat employs polyisocyanate crosslinking agent.

Background Art

Recently, there has been interest in the use of rubbery resilient materials for areas which are subject to mechanical shock such as automobile bumpers, moldings and front ends. The use of such materials aids in providing protection from permanent structural damage but, in order to attain the desired appearance, a protective coating must have unique properties, such as a high degree of extensibility, impact resistance, resistance to cracking under severe environmental conditions, such as exposure to low temperature and low humidity. Conventional coatings, including those employed on rubber and similar extensible



- 2 -

objects heretofore, do not have the required combination of properties. Generally compositions that are flexible enough to be applied over both metal and plastic substrates have rather poor weatherability and overall durability.

5 U.S. Patent 3,882,189 and U.S. Patent 3,962,522 are exemplary of numerous patents which describe flexible coating compositions wherein the resin comprises polyurethane modified polyesters formed by reacting polyisocyanate with polyester polyols. These resins are
10 cured with amine aldehyde crosslinkers. It is taught therein, that the presence of the urethane groups in the polymer significantly contributes to the flexibility as well as improved weathering properties, gloss, and abrasion resistance of the coating. However, while it is thus
15 desirable to employ a substantial number of urethane groups in these resins, the amount which may be included in these types of resins is limited. When hydroxy polyester resin is reacted with polyisocyanate it has a tendency to form a gelled mass and thus the amount of polyisocyanate that may
20 be employed must be restricted in order to avoid gelation. Still further, these urethane linkages are added in a latter modification of the polyester polyol reaction product, rather than being incorporated into the backbone of the resin.

25 Disclosure of the Invention

This invention is directed to a flexible basecoat/clearcoat coating composition which is suitable for use over various substrates, including rubbery, resilient materials as well as metal. The
30 basecoat/clearcoat coating composition of this invention is characterized in that the basecoat composition and the clearcoat composition each independently comprises:



- 3 -

(A) hydroxy-containing urethane modified polyester (i) having a number average molecular weight ($\overline{M}_n$) of between about 1000 and about 10,000, (ii) having a hydroxyl number of between about 30 and about 200, and (iii) containing
5 between about 1 and about 10 urethane groups per molecule, and being made from reactants comprising:

- (1) urethane modified diol made by reacting:
 - (a) diol,
 - (b) diisocyanate,
10 wherein the diol and diisocyanate are reacted in a molar ratio of from about 4:1 to about 4:3;
- (2) polyol comprising at least about 5 weight percent triol; and
- (3) acid component selected from dicarboxylic acids
15 and anhydrides thereof;

(B) crosslinking agent; and

(C) 0-60 weight percent, based on the total weight of (A) and (B) of the composition, of a linear polyurethane having a number average molecular weight of between about 15,000
20 and about 40,000, preferably of between about 20,000 and about 30,000. The basecoat composition additionally comprises pigment.

The crosslinking agent of the clearcoat composition of this invention is a polyisocyanate
25 crosslinking agent. The crosslinking agent of the basecoat composition of this invention is an amine-aldehyde crosslinking agent.

Advantageously, the flexible basecoat/clearcoat coating compositions of the invention of this application
30 possess superior weathering properties as well as excellent adhesion to metal and plastic, thus making them well suited for use as coatings on various car components. In forming



- 4 -

the hydroxy-containing urethane modified polyester of the clearcoat, the urethane linkages are advantageously incorporated into the backbone of the modified polyester, since they are formed in an initial reaction of diisocyanate with the diol, rather than being incorporated into the polyester in a later reaction step as is done when forming prior art urethane polyester resins. It has now been found that the initial incorporation of the urethane linkage into the backbone of the modified polyester allows the formation of more flexible coatings with improved weathering properties, particularly suitable to form automotive basecoat/clearcoat coatings.

Still further, the ability to use of the same coating compositions on metal and plastic components in car production offers distinct commercial advantages, particularly in terms of production efficiency. Additionally, because this system can be employed on metal as well as plastic components, the problem of color matching, which must be resolved when using a different coating on the metal and plastic, is eliminated.

Best Mode for Carrying Out The Invention

This invention is directed to flexible basecoat/clearcoat coating compositions, wherein the basecoat composition and the clearcoat composition comprise hydroxy-containing urethane modifying polyester and crosslinking agent. The basecoat composition crosslinking agent is amine-aldehyde while the clearcoat composition crosslinking agent is polyisocyanate. The basecoat composition additionally comprises pigment. Optionally, the basecoat composition and/or the clearcoat composition may include a high molecular weight linear polyurethane. The novel hydroxy-containing urethane modified polyester is made from urethane modified diols reacted with polyol and



- 5 -

diacid component. The various components of the compositions of this invention will be discussed in detail.

The hydroxy-containing urethane modified polyester of the basecoat/clearcoat coating composition of this invention has a number average molecular weight ($\overline{M}_n$) of between about 1000 and about 10,000, preferably between about 2000 and about 4000. This modified polyester has a hydroxyl number of between about 30 and about 200, preferably between about 50 and about 120. It also contains between about 1 and about 10 urethane groups per molecule. One of the reactants used to form the hydroxy-containing urethane modified polyester is a urethane modified diol which is made by reacting diol and diisocyanate. In forming this urethane modified diol, the diol and the diisocyanate are reacted in a molar ratio of from about 4:1 to about 4:3, preferably in a molar ratio of from about 2:1.8 to about 2:1.2, most preferably in about a 2:1 molar ratio. The diols employed in making the urethane modified diol include, but are not limited to, alkylene glycols, such as butylene glycol, neopentyl glycol, 1,5-pentene glycol, 3-cyclohexene-1,1-dimethynol, and other glycols such as hydrogenated bisphenol A, caprolactone diol (i.e., the reaction product of caprolactone and ethylene glycol), hydroxy alkylated bisphenols, polyether glycols, e.g., poly(oxytetramethylene) glycol, polyester diols, e.g., 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, and the like. Preferred diols are neopentyl glycol and 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, the latter material being commercially available as Esterdiol 204 (a trademark of and available from Union Carbide, New York, N.Y.). While a number of types of diols have been mentioned above as suitable for use as the diol component in making the urethane modified diol of this invention, their disclosure is not meant to be



- 6 -

limiting. A great many diols are known in the art. Selection of other diols which would be suitable for use in forming the urethane modified diol would be well within the skill of those in the art. Mixtures of diols may also be
5 employed to make the urethane modified diol.

The diisocyanate employed in making the urethane modified diol may be essentially any diisocyanate. Many such organic diisocyanate are known in the art. Suitable diisocyanates include hydrocarbon diisocyanate or
10 substituted hydrocarbon diisocyanate, such as 1,6-hexamethylene diisocyanate, isophorone diisocyanate, p-phenylene diisocyanate, biphenyl diisocyanate, toluene diisocyanate, and 3,3-dimethyl-4,4-biphenylene diisocyanate. While the diisocyanate may be any of a
15 number of aliphatic, cycloaliphatic, and aromatic diisocyanates, it is preferred that the diisocyanate be an aliphatic diisocyanate, such as 4,4-dicyclohexylmethane-diisocyanate. As would be apparent to those skilled in the art, mixtures of various diisocyanates may also be employed
20 at the diisocyanate component used in forming the urethane-modifying diol.

The polyol component used in forming the hydroxy-containing urethane modified polyester of the basecoat/clearcoat compositions comprise at least about 5
25 weight percent triol (based on the weight of the polyol component). Preferred triols are conventional low molecular triols such as 1,2,6-hexene triol, 1,1,1-trimethylol propane, pentaerythritol, 3-(2-hydroxy-propoxy)-1,2-propanediol and polycaprolactone triols, which
30 are commercially available as, for example PCP-301 (trademark, Union Carbide Corp., New York, N.Y.). This polyol component may also comprise, in addition to the triols other polyol materials such as diols or tetrols. Preferably, however, these other polyols, when employed,



- 7 -

consist of diols. Examples of suitable diols which may be included in the polyol component are those which have been disclosed above as a component for forming the urethane modified diol. While the polyol component may comprise materials such as a diol in addition to the triol, the polyol component may consist essentially of triols. By employing diols in the polyol component in addition to the triols the flexibility of the coating composition is generally increased. Thus selection of the polyol component to be used in forming the hydroxy-containing urethane modified polyester of the clearcoat will be dependent on the particular desired properties and application of the coating composition. When diols are employed in the polyol component, the polyol preferably comprises from about 10 to about 80 weight percent triols and from about 90 to about 20 weight percent diols.

The acid component which is used to form the modified polyester of the compositions of this invention comprises aliphatic, aromatic, cycloaliphatic dicarboxylic acid or anhydrides. Preferred dicarboxylic acids are the $C_6 - C_{12}$ acids, which include adipic, azelaic, sebacic, or dodecane dicarboxylic acid, or cyclohexanedicarboxylic acid. More preferably, the dicarboxylic acids employed are aliphatic dicarboxylic acids, most preferably, additionally being linear. Mixtures of suitable acids and/or their anhydrides may also be used as the acid component in this invention.

In forming the coating compositions of this invention, the diol (a) and the diisocyanate (b) described above are combined and reacted, generally at an elevated temperature so as to form the urethane modified diol. The ratio of the diol to diisocyanate (i.e., a molar excess of diol) has been chosen so that at the completion of this reaction no free isocyanates are present, having been



- 8 -

incorporated into a hydroxy functional material. This urethane modified diol is then combined and reacted with the polyol and acid components, generally in the presence of a catalyst and at elevated temperatures, so as to effect
5 formation of a hydroxy-containing urethane modified polyester. Suitable catalysts for the carboxy/hydroxy condensation reaction include such catalysts as tetraisopropyl titanate, strong acids such as p-toluene phosphonic acid, phosphoric acid sulfuric acid and materials
10 such as zinc oxide, antimony oxide (Sb_2O_3) and sodium acetate. Other catalysts will be apparent to those skilled in the art.

The reactions, whereby the hydroxy-containing urethane modified polyesters of the basecoat or clearcoat
15 are formed, are generally carried out in the presence of solvents commonly employed for coating formulations such as toluene, xylene, methyl amyl ketone, etc.

The hydroxy-containing urethane modified polyester of the basecoat coating composition and the clearcoat
20 coating composition employed in the basecoat/clearcoat system may be similar or different embodiments of this polyester. Selection of the particular modified polyester to be employed in the coatings would be dependent on the particular properties and application of the coatings
25 desired. Such selection will be well within the skill of one in the art.

The crosslinking agent of the clearcoat coating composition of the invention is a polyisocyanate crosslinking agent, i.e., a compound having 2 or more,
30 preferably 3 or more, reactive isocyanate groups per molecule. These polyisocyanate materials function as a crosslinking agent in the composition of the invention by reaction with the hydroxyl functionality of the hydroxy containing urethane modified polyester (A) and by reaction



- 9 -

with the hydroxyl functionality on the linear polyurethane if such linear polyurethane is included in the composition. This polyisocyanate crosslinking agent is generally included in the clearcoat coating composition of the invention in an amount of between about 5 and about 60, more preferably between about 20 and about 40 weight percent based on the weight of the hydroxy-containing urethane modified polyester of the clearcoat composition. Selection of the optimal amount of polyisocyanate crosslinking agent to be employed in the coating composition is dependent on the desired properties (e.g., flexibility) as well as its intended use and selection of such amount would be within the skill of one in the art.

Polyisocyanates are well known in the art and numerous suitable organic isocyanates having 2 or more reactive isocyanate groups per molecule will be apparent to those skilled in the art. Among the many suitable polyisocyanates are aliphatic, cycloaliphatic and aromatic isocyanate compounds. Representative of the numerous isocyanates which may be employed are (1) aliphatic diisocyanates such as trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, 1,2 propylene diisocyanate, 1,2 butylene diisocyanate, 2,3 butylene diisocyanate, 1,3 butylene diisocyanate, 1,3 butylene diisocyanate, ethylidene diisocyanate, butylidene diisocyanate, 4,4'-bis-(isocyanate hexyl) methane, bis(2-isocyanate-ethyl) fumarate, 2,6-diisocyanate methyl caproate, 2,2,4(2,4,4)-trimethylhexamethylene diisocyanate, and dimer acid diisocyanates; (2) cycloaliphatic diisocyanates such as 1,3 cyclopentane diisocyanate, 1,4 cyclopentane diisocyanate, 1,2 cyclopentane diisocyanate, and methylcyclohexylene diisocyanate; (3) aromatic diisocyanates such



- 10 -

as m-phenylene diisocyanate, p-phenylenediisocyanate, 4,4'diphenyl diisocyanate, 1,5 methylene diisocyanate, 1,4 naphthalene diisocyanate; (4) aliphatic/aromatic diisocyanates such as 4,4'diphenylene methane diisocyanates, 2,4 or 2,6 tolulene diisocyanate, 4,4'toluidene diisocyanate, 1,4 xylylene diisocyanate; (5) nuclear substituted aromatic compounds such as dianisidine diisocyanate, 4,4'diphenylether diisocyanate, chloro-diphenylene diisocyanate; (6) triisocyanates such as triphenylmethane 4,4', 4,4" triisocyanate, 1,3, 5 triisocyanate benzene, 2,4, 6 triisocyanate toluene; (7) tetraisocyanates such as 4,4' diphenyl dimethylmethane 2,2',5,5' tetraisocyanate; (8) polymerized isocyanates such as tolylene diisocyanate dimers and trimers and the like; and (9) polyisocyanates such as prepolymers derived from a polyol, including polyether polyols or polyester polyols (including polyethers which are reacted with excess polyisocyanates to form isocyanate terminated prepolymers), simple polyols such as glycols (e.g., ethylene glycol, propylene glycol), other polyols such as glycerol, trimethylol propane, hexane triol, pentaerythritol and the like, as well as monoethers, e.g., diethylene glycol, tripropylene glycol and the like and polyethers, i.e., alkylene oxide condensates of the above. While the polyisocyanate may be any organic polyisocyanate, such crosslinking agents for coating composition to be employed as topcoats are preferably aliphatic or cycloaliphatic polyisocyanates due to their superior weathering properties.

Especially preferred for use in the clearcoat compositions of the invention are trimerized products of aliphatic diisocyanates such as 1,6 hexamethylene diisocyanate. Still another particularly preferred type of a polyisocyanate crosslinking agent for the clearcoat is a



- 11 -

polyisocyanate having a biuret structure. This type of polyisocyanate is well known as are methods for making the same. One such polyisocyanate crosslinking agent is a high molecular weight biuret of 1,6 hexamethylene diisocyanate sold by Mobay Chemical Company under the tradename Desmodur N. Exemplary of other biuret type polyisocyanates are those prepared in accordance with U.S. Patent 3,976,622 to Wagner et al.

The crosslinking agent of the basecoat coating composition of this invention is an amine-aldehyde crosslinking agent. Amine-aldehyde crosslinking agents suitable for crosslinking hydroxy functional bearing materials are well known in the art. Typically, these crosslinking materials are product of reactions of melamine, or urea with formaldehyde and various alcohols containing up to and including 4 carbon atoms. Preferably, the amine-aldehyde crosslinking agents useful in this invention are amine-aldehyde resins such as condensation products of formaldehyde with melamine, substituted melamine, urea, benzoguanamine or substituted benzoguanamine. Preferred members of this class are methylated melamine-formaldehyde resins such as hexamethoxymethylmelamine. The particular preferred crosslinkers are the high solids melamine resins which has substantially 100 percent nonvolatile content as measured by the foil method at 45 °C for 45 minutes. For the purposes of the preferred composition of this invention it should be recognized that it is important not to introduce extraneous diluents that lower the final solids content of the coating. Other suitable amine-aldehyde crosslinking agents will be apparent to one skilled in the art. The amine-aldehyde materials function as a crosslinking agent in the basecoat compositions of the invention by reacting with the hydroxy functionality of the hydroxy-containing



- 12 -

urethane modified polyester (A) of the basecoat composition and by reaction with the hydroxy functionality on the linear polyurethane (C), if such materials are included in the basecoat compositions. The amine aldehyde crosslinking agent is generally included in the basecoat composition in an amount of between about 5 and about 60, more preferably, between about 20 and about 40 weight percent based on the weight of the hydroxy-containing urethane modified polyester. Selection of the particular amount of amine-aldehyde crosslinking agent to be employed in the basecoat composition is dependent on the desired properties of the coating compositions as well as its intended use as would be apparent to one skilled in the art.

Particular preferred crosslinking agents are the amino crosslinking agents sold by American Cyanamid under the trademark "Cymel". In particular, Cymel 301, 303, 325, 1130, 1156, which are alkalated melamine aldehyde resins are useful in the compositions of this invention. The crosslinking reactions are catalytically accelerated by acids. One such catalyst for example which may be so employed is p-toluene sulfonic acid which, when employed, is generally added to the composition in about .5% by weight based on the total weight of the amine-aldehyde crosslinker and hydroxy-containing modified polyester of the basecoat composition.

The amounts of crosslinking agent to be employed in the basecoat composition and in the clearcoat composition are selected individually, i.e., the weight percent amounts of crosslinker employed in the basecoat composition and in the clearcoat composition of a particular basecoat/clearcoat system may be different or be similar.

The basecoat coating composition of the invention also include pigments, as noted above. A wide variety of



- 13 -

pigments are available and known for use in coating compositions by those skilled in the art. Selection of the optimal amount of pigment to be included in the basecoat composition would be dependent on, e.g., desired color, hiding requirements of the coating, etc., and would be within the skill of those in the art.

Optional Materials

Additional materials which may be employed in the coating compositions of this invention include a high molecular weight linear polyurethane which has a number average molecular weight of between about 15,000 and about 40,000, preferably between about 20,000 and about 30,000. It may be made by reacting one of the above mentioned diisocyanates and diols, such as oligoester diol, polycaprolactone diol, polyoxypropylene diol, polyether diols, etc. Suitable high molecular weight linear polyurethane materials are commercially available, for example, as Spenlite L06-30S, (available from and a trademark of Spencer-Kellogg, Buffalo, N.Y.). The high molecular weight polyurethane may be employed in the composition in amounts up to about 60 weight percent based on the total weight of the hydroxy-containing urethane modified polyester and crosslinking agent. When employed, it is preferred that they be included in the composition in amounts of between about 10%-60%, more preferably 30%-50% by weight as described. It has been found that by incorporating this polyurethane in the basecoat of basecoat/clearcoat systems, the depth of color and metallic glamour of the basecoat/clearcoat system is improved. While this linear polyurethane, when employed, is generally preferably only included in the basecoat composition, it



- 14 -

may be employed in either or both coats and the amounts are independently selected.

In addition to the above discussed components, other materials may be included in the coating compositions of this invention. These include materials such as catalysts, antioxidants, U.V. absorbers, solvents, surface modifiers and whitening agents. Solvents used in the coating composition of this invention are those which are commonly used, e.g., to facilitate spray application and high solids content and include toluene, xylene, methylethyl ketone, acetone, 2-ethoxy-1-ethanol, diacetone alcohol, tetrahydrofuran, ethyl acetate, dimethylsuccinate, dimethylglutarate, dimethyladipate or mixtures thereof. The solvent in which the hydroxy-containing urethane modified polyester is prepared may be employed as a solvent for the composition thus eliminating the need for drying the resin after preparation, if such is desired.

Typical of the ultraviolet stabilizers that are useful in this invention are benzophenones such as dodecyl oxibenzophenone, 2,4-dihydroxybenzophenone, hydroxybenzophenones containing sulfonic groups, 2-4-dihydroxy-3'5'-ditertiary butyl benzophenone, 2,2',4', trihydroxy benzophenone esters of dicarboxylic acids, 2-hydroxy-4-acryloxyethoxybenzophenone, aliphatic mono esters of 2,2',4-trihydroxy-4' alkoxybenzophenone; 2-hydroxy-4-methoxy-2-carboxybenzophenone; triazoles such as 2-phenyl-4-(2'4'-dihydroxybenzoyl) - triazoles substituted benzotriazoles such as hydroxy-phenyltriazoles such as 2-(2'-hydroxy-5'-methylphenyl) benzotriazole, 2-(2'-hydroxy-phenyl) benzotriazole, 2-(2'-hydroxy-5'-octylphenyl) naphthiotriazole. Another type of ultraviolet stabilizer and one that is particularly preferred for use in the coatings of this invention comprise those taught in



- 15 -

concurrently filed U.S. application Serial No. _____
entitled " Polymeric Light Stabilizers" to Kordomenos et
al. These stabilizers contain the sterically hindered
polyalkylpiperidine radical and at least two primary
5 hydroxyl groups available for reacting with the
crosslinking agent, e.g., amine-aldehyde or
polyisocyanate, of the coating composition.

Typical of the antioxidants which may be employed
in the coating composition include tetrakis alkylene
10 (di-alkyl hydroxy aryl) alkyl ester alkanes such as
tetrakis methylene 3(3',5'-dibutyl-4'hydroxyphenyl)
propionate methane, reaction product of p-amino
diphenylamine and glycidyl methacrylate, reaction product
of n-hexyl-N'-phenylamine diamine and glycidyl
15 methacrylate, pentaerythritol tetrakis (thioglycolate),
trimethylol propane tris (thioglycolate), trimethylol
ethane tris(thioglycolate), N-(4-anilino phenyl) acrylamide,
N-(4-anilinophenyl) maleamic acid N-(4-anilinophenyl)
maleimide, alkylhydroxyphenyl groups bonded through
20 carboalkoxy linkages to nitrogen atom of a heterocyclic
nucleus containing an imidodicarbonyl group or an
imidodithiocarbonyl group, 3,3 di tert, butyl-4-hydroxy
cinnamionitrile, ethyl 3,5-di tert, hexyl-4-hydroxy-
cinnamate, substituted benzyl esters of B-substituted
25 hydroxy phenyl) propionic acids, bis (hydroxyphenyl
alkylene) alkyl isocyanurate compounds, tetrakis hydroxy
benzyl phosphonium halides alone or in combination with a
dialkylthiodialkanoate, thioeimethylidene tetrakisphenols
alone or in combination with a dialkyl thiodialkanoate or
phosphite or phosphonate, dihydrocarbyl-hydroxy phenyl aryl
30 or alkyl phosphonites or phosphonates or phosphates or
phosphites or phosphinates or phosphonites or
phosphorothionates or phosphinothionates, diphenyl



- 16 -

bis(3,5-di-tert-butyl-4-hydroxy) silane, hydrocarbyl-hydroxyphenyl-dihydrocarbyldithio-carbamates such as 3,5 di-tert-butyl-4-hydroxy phenyl dimethyldithio carbamate and amino benzyl thioether.

5 In one preferred embodiment of basecoat/clearcoat compositions, the basecoat would preferably contain a benzotriazole U.V. stabilizer such as Tinuvin 328 (a trademark of and commercially available from Ciba-Geigy, Ardsley, N.Y.), and the clearcoat would contain a
10 benzotriazole U.V. stabilizer, e.g., Tinuvin 328, the polymeric hindered amine light stabilizer of the aforementioned concurrently filed application to Kordomenos et al, and an antioxidant, e.g., Irganox-1010. (available from and a trademark of Ciba-Geigy). While preferred
15 combinations of stabilizer and antioxidant have been described, these teachings are not meant to be limiting. Selection of the optimal type of stabilizer and antioxidant which may be employed would be within the skill of one in the art.

20 Surface modifiers or wetting agents are common additives for liquid paint compositions. Exact mode of operation of these surface modifiers is not known but it is thought that their presence contributes to better adhesion of coating compositions to the surface being coated and
25 helps formation of thin coatings, particularly on metal surfaces. The choice of surface modifiers or wetting agents is dependent upon the type of surface to be coated. Selection of appropriate surface modifiers will be well within the skill of the artisan. Typical of these surface
30 modifiers are polybutyl acrylate and a wide variety of silicon wetting agents which are commercially available.

For many applications of the coating compositions of the invention, particularly high solids compositions, it



- 17 -

may be desirable to employ flow control additives to provide sag free coatings. Among numerous such materials are NAD's such as described by Porter (S. Porter, Jr., and B.N. McBane, U.S. Patent 4,025,474, May 24, 1977). These
5 particle dispersions may be included generally in amount up to 15% by weight of the total composition. Other types of NAD's such as described by D.L. Maker and S.C. Peng (U.S. Patent 3,814,721, June 4, 1974) or by S.K. Horvath (U.S. application Serial No. 292,853, filed August 14, 1981) also
10 may be included in the coating compositions.

The coating composition can be applied by conventional methods known to those in the art. These methods include roll coating, spray coating, dipping or brushing and of course the particular application technique
15 chosen with the particular substrate to be coating and the environment in which coating operation takes place.

Particular preferred techniques for applying these coating compositions, particularly when applying the same to automobiles, is spray coating through the nozzle of the spray gun. The basecoat can be applied as a single
20 component by means of a single component spray gun. On the other hand, in spray applying the clearcoat composition, the hydroxyl-containing urethane modified polyester and the optional linear polyurethane along with other additives such as pigments, U.V. absorbers, antioxidants and other
25 nonreactive materials are admixed with a solvent. These materials are fed as one component of a two component system into a spray gun which combines the materials as they are sprayed onto the automotive substrate. The other material is the polyisocyanate crosslinking agent, which
30 may or may not be cut with a suitable nonreactive solvent.



- 18 -

Industrial Applicability

It will be apparent from the foregoing that this invention has industrial applicability to automotive application and provides a flexible durable coating for metal and plastic substrates.

The invention will be further understood by referring to the following detailed examples. It should be understood that the specific examples are presented by way of illustration and not by way of limitation. Unless otherwise specified, all references to "parts" is intended to mean parts by weight.

Example I

In a suitable reactor 562 gms of Esterdiol-204 (trademark of Union Carbide), 360 gms of xylene were charged. The mixture was brought to reflux (149°C) and any water present was stripped out. The temperature was lowered to 93°C and 360 gms of Desmondur W (trademark of Mobay Chemical Co.) was added dropwise in a period of one hour. After the end of the addition, the mixture was postreacted at 93°C until no NCO group was observed in an infrared spectrum. At this point, 240 gms of PCP-0301 (polycaprolactone triol, trademark of Union Carbide, New York, N.Y.) 263 gms of adipic acid, 3 gms of dibutyl tin oxide, and 215 gms of xylene were added. The mixture was heated up to 204°C and water was distilled off until the acid number dropped below 10. The batch was then thinned with 480 parts of methyl amyl ketone. The final product had η_{sp}/c viscosity at 70.8% NV and acid number 1.2.



- 19 -

Example II

In a suitable reactor 562 gms of Esterdiol-204 (trademark of Union Carbide) and 360 gms of xylene were charged. The mixture was brought to reflux (149°C) and any water present was stripped out. The temperature was lowered to 93°C and 360 gms of isophorone diisocyanate was added dropwise in a period of one hour. After the end of the addition, the mixture was postreacted at 93°C until no NCO group was observed in an IR spectrum. At this point, 240 gms of PCP-0301 (polycaprolactone triol, trademark of Union Carbide, New York, N.Y.) 263 gms of adipic acid, 3 gms of dibutyl tin oxide, and 215 gms of xylene were added. The mixture was heated up to 204°C and water was distilled off until the acid number dropped below 10. The batch was then thinned with 480 parts of methyl amyl ketone. The final product had η viscosity at 72% NV and acid number 7.9.

Example III

In a suitable reactor 286 gms of neopentyl glycol and 360 gms of xylene were charged. The temperature was roused to 93°C and 360 gms of Desmondur W (trademark of Mobay Chemical Co.) was added dropwise in a period of one hour. After the end of the addition, the mixture was postreacted at 93°C until no NCO group was observed in an IR spectrum. At this point, 240 gms of PCP-0301 (polycaprolactone triol, trademark, of Union Carbide) 263 gms of adipic acid, 3 gms of dibutyl tin oxide, and 215 gms of xylene were added. The mixture was heated up to 204°C and water and xylene was distilled off until the acid number dropped below 10. The batch was then thinned with 480 parts of methyl amyl ketone. The final product had η viscosity at 71.7% NV and acid number 0.8. number.



- 20 -

Example IV

In a suitable reactor 281 gms of Esterdiol-204, 728 gms of PCP-0200, (polycaprolactone diol, trademark, Union Carbide) and 360 gms of xylene were charged. The mixture was brought to reflux (149°C) and any water present was stripped out. The temperature was lowered at 93°C and 360 gms of Desmondur W (trademark of Mobay Chemical Co.) was added dropwise in a period of one hour. After the end of the addition, the mixture was postreacted at 93°C until no NCO group was observed in an IR spectrum. At this point, 108 gms of trimethylol propane, 263 gms of adipic acid, 3 gms of dibutyl tin oxide, and 200 gms of xylene were added. The mixture was heated up to 204°C and water and xylene was distilled off until the acid number dropped below 10. The batch was then thinned with 400 parts of methyl amyl ketone. The final product had η_{sp} viscosity at 72.7% NV and acid number 2.0.

Example V

In a suitable reactor 562 gms of Esterdiol-204 (trademark of Union Carbide) and 360 gms of xylene were charged. The mixture was brought to reflux (149°C) and any water present was stripped out. The temperature was lowered to 93°C and 360 gms of Desmondur W (trademark of Mobay Chemical Co.) was added dropwise in a period of one hour. After the end of the addition, the mixture was postreacted at 93°C until no NCO group was observed in an IR spectrum. At this point, 108 gms of trimethylol propionic and 108 gms of dimer acid (Empol 1016, Emery, Ind.) 3 gms of dibutyl tin oxide, and 200 gms of xylene were added. The mixture was heated up to 204°C and water



- 21 -

and xylene was distilled off until the acid number dropped below 10. The batch was then thinned with 400 parts of methyl amyl ketone. The final product had X+ viscosity at 69.2% NV and acid number 2.9.

5

Example VI

In a suitable reactor 753 gms of Esterdiol-204 (trademark of Union Carbide) and 360 gms of xylene were charged. The mixture was brought to reflux (149°C) and any water present were stripped out. The temperature was
10 lowered to 93°C and 360 gms of Desmondur W (trademark of Mobay Chemical Co.) was added dropwise in a period of one hour. After the end of the addition, the mixture was postreacted at 93°C until no NCO group was observed in an IR spectrum. At this point, 474 gms of PCP-0301
15 (polycaprolactone triol, trademark of Union Carbide) 263 gms of adipic acid, 402 gms of dodecanoic acid, 4 gms of dibutyl tin oxide, and 200 gms of xylene were added. The mixture was heated up to 204°C and water and xylene was distilled off until the acid number dropped below 10. The
20 batch was thinned with 480 parts of methyl amyl ketone. The final product of Z₁+ viscosity at 70.0% NV and acid number 5.2.

Example VII

In a suitable reactor 136 gms of propylene glycol,
25 172 gms of adipic acid and 66.4 gms of toluene were added. The mixture was heated up to reflux and 42.6 gms of water were stripped. At this point, 321 gms of oligoester (made according to Example I of U.S. Patent 4,322,508 to Peng et al), 250 gms of toluene, 10 gms of dibutyl tin dilaurate
30 were added. In a period of 3 hours, 396 parts of Desmondur W (trademark, Mobay Chemical Co.) were added. During the



- 22 -

addition, the temperature was let to rise from 116°C to 143°C. The mixture was kept at this temperature until no NCO pick was observed in an IR spectrum. The batch was thinned with 860 gms of toluene and 1,260 gms isopropanol. 5 The final product had a weight viscosity at 33.1% NV.

Example VIII

10 In a suitable reactor 562 gms of Esterdiol-204 (trademark of Union Carbide) and 360 gms of xylene were charged. The mixture was brought to reflux (149°C) and any water present was stripped out. The temperature was lowered to 93°C and 360 gms of Desmondur W (trademark of Mobay Chemical Co.) was added dropwise in a period of one hour. After the end of the addition, the mixture was postreacted at 93°C until no NCO group was observed in an 15 IR spectrum. At this point, 240 gms of PCP-0301 (polycaprolactone triol, trademark of Union Carbide, New York, N.Y.) 131 gms of adipic acid and 133 gms of phthalic anhydride, 3 gms of dibutyl tin oxide, and 215 gms of xylene were added. The mixture was heated up to 204°C and 20 water was distilled off until the acid number dropped below 10. The batch was then thinned with 480 parts of methyl amyl ketone. The final product had Z₅ viscosity at 70.1% NV and acid number 3.



- 23 -

Examples IX - XII

Flexible basecoat compositions were formulated according to the following table:

<u>Compositions/Example</u>		<u>IX</u>	<u>X</u>	<u>XI</u>	<u>XII</u>
5	Resin of Example I	50			
	Resin of Example II		93		
	Resin of Example III			50	
	Resin of Example VII			100	
	Resin of Example IV				57
10	Spenlite L06-30S ¹	100			50
	Cymel 1130 ²	46	46	46	46
	Tinuvin-328 ³	3.6	3.6	3.6	3.6
	PTSA (40%)	1.5	1.5	1.5	1.5
	5000-AR ⁴	50	50	50	49
15	Xylene	75	75	75	
	Isopropyl alcohol	75	75	75	75
	Surfynol-104 ⁵	6	6	6	21
	Methyl amyl ketone				100

The above basecoats were produced to 20 sec. at #4 Ford Cup with methyl amyl ketone before spraying.

¹Trademark, Spencer-Kellogg, Buffalo, N.Y.

²Trademark, American Cyanamid Co., Wayne, N.J.

³Trademark, Ciba-Geigy

⁴Aluminum Paste, purchased Silberling, Lansford, Pa.

⁵Trademark, Air Products and Chemicals, Inc., Allentown, Pa. (Surfactant: 2,4,7,9-tetramethyl-5-decyn-4,7-diol)



- 24 -

Clearcoat Compositions

Examples		XIII	XIV	XV	XVI	XVII	XVIII	XIX
Composition								
	Resin of Example I	414						
5	Resin of Example II		401					
	Resin of Example III			403				
	Resin of Example IV				397			
	Resin of Example V					417		
	Resin of Example VI						414	
10	Resin of Example VIII							414
	Desmondur L-2291A ¹	123		123	123	123	123	123
	Desmondur Z-4370 ²	175	175					175
	Tinuvin-328 ³	6.2	6.2	6.2	6.2	6.2	6.2	6.2
	Polymeric light stabilizer	8.8	8.8	8.8	8.8	8.8	8.8	8.8
15	Irganox 1010 ⁵	0.8	0.8	0.8	0.8	0.8	0.8	0.8
	Methyl amyl ketone	100	100	100	100	100	100	100

The above compositions were reduced to 30 sec. viscosity at #4 Ford Cup with methyl amyl ketone.

20 ^{1,2}Trademark, Mobay Chemical Co., Pittsburgh, Pa.

³Trademark, Ciba-Geigy

⁴Hindered amine stabilizer made according to Example I of U.S. Application S.N. _____ to Kordomenos et al.

⁵Trademark, Ciba-Geigy (Antioxidant)



Example XX - XXIX

The following basecoat/clearcoat coating composition were sprayed over metal and plastic substrates and cured for 30 minutes at 121°C.

Example XX XXI XXII XXIII XXIV XXV XXVI XXVII XXVIII XXIX

Coating Composition

Basecoat of Example	IX	X	XI	XII	IX	IX	IX	IX	IX	IX	IX	IX
Clearcoat of Example	XIII	XIV	XIII	XIII	XIV	XV	XVI	XVII	XVIII	XIX		
% Elongation	150	155	120	140	208	160	140	130	135	50		
MER resistance (100 rubs)	Excell	Excell	Excell	Excell	Excell	Excell	Good	Excell	Excell	Excell		
QUV (1000 hrs.)	Excell	Excell	Excell	Excell	Excell	Excell	Good	Excell	Excell	Excell		

- 26 -

1. A flexible basecoat/clearcoat coating composition, useful as automotive finish coats on metal and plastic substrates, which is characterized in that the basecoat composition and the clearcoat composition each independently comprises:

(A) hydroxy-containing urethane modified polyester (i) having a number average molecular weight ($\overline{M}_n$) of between about 1000 and about 10,000, (ii) having a hydroxyl number of between about 30 and about 200, and (iii) containing between about 1 and about 10 urethane groups per molecule, and being made from reactants comprising:

- (1) urethane modified diol made by reacting:
 - (a) diol, and
 - (b) diisocyanate,wherein said diol and said diisocyanate are reacted in a molar ratio of from about 4:1 to about 4:3;
- (2) polyol comprising at least about 5 weight percent triol; and
- (3) acid component selected from dicarboxylic acids and anhydrides thereof; and

(B) crosslinking agent; and

(C) 0-60 weight percent, based on the total weight of (A) and (B) of the composition, of a linear polyurethane having a number average molecular weight of between about 15,000 and about 40,000, and

wherein said crosslinking agent of said clearcoat composition is a polyisocyanate crosslinking agent and said crosslinking agent of said basecoat composition is an amine-aldehyde crosslinking agent, and wherein said basecoat composition additionally comprises pigment.



- 27 -

2. A flexible basecoat/clearcoat coating composition according to claim 1, wherein said hydroxy-containing urethane modified polyester of said clearcoat composition has a number average molecular weight of between about 2000 and about 4000.

3. A flexible basecoat/clearcoat coating composition according to claim 1, wherein said hydroxy-containing urethane modified polyester of said clearcoat composition has a hydroxyl number of between about 50 and about 120.

4. A flexible basecoat/clearcoat coating composition according to claim 1, wherein in forming said urethane modified diol of said clearcoat composition said diol and said diisocyanate are reacted in a molar ratio of from about 2:0.8 to about 2:1.2.

5. A flexible basecoat/clearcoat coating composition according to claim 1, wherein said polyol of said clearcoat composition further comprises diol.

6. A coating composition according to claim 5, wherein said polyol of said clearcoat comprises about 10-80 weight percent triol and about 80-20 weight percent diol.

7. A flexible basecoat/clearcoat coating composition according to claim 1, wherein said dicarboxylic acids of said clearcoat composition comprise C₆ - C₁₂ aliphatic dicarboxylic acid.



- 28 -

8. A flexible basecoat/clearcoat coating composition according to claim 1, wherein said polyisocyanate crosslinking agent is included in said clearcoat composition in an amount of between about 5 and
5 about 60 weight percent based on the weight of the hydroxy-containing urethane modified polyesters of the clearcoat composition.

9. A coating composition according to claim 1, wherein said polyisocyanate crosslinking agent of said clearcoat composition is a diisocyanate.

10. A coating composition according to claim 1, wherein said polyisocyanate crosslinking agent of said clearcoat composition has 3 or more reactive isocyanates per molecule.

11. A coating composition according to claim 10, wherein said polyisocyanate crosslinking agent is a trimerized product of an aliphatic diisocyanate.

12. A coating composition according to claim 11, wherein said polyisocyanate crosslinking agent is a trimerized reaction product of 1,6 hexamethylene diisocyanate.

13. A coating composition according to claim 10, wherein said polyisocyanate crosslinking agent is a polyisocyanate having a biuret structure.



- 29 -

14. A flexible basecoat/clearcoat composition according to claim 1, wherein said hydroxy-containing urethane modified polyester of said basecoat composition has a number average molecular weight (M_n) of between about
5 2000 and about 4000.

15. A flexible basecoat/clearcoat coating composition according to claim 1, wherein in forming said urethane modified diol of said basecoat composition said diol and said diisocyanate are reacted in a molar ratio of
5 from about 2:0.8 to about 2:1.2.

16. A flexible basecoat/clearcoat coating composition according to claim 1, wherein said polyol of said basecoat composition further comprises diol.

17. A flexible basecoat/clearcoat coating composition according to claim 16, wherein said polyol of said basecoat composition comprises about 10-80 weight percent triol and about 80-20 weight percent diol.

18. A flexible basecoat/clearcoat coating composition according to claim 1, wherein said dicarboxylic acids of said basecoat composition comprise $C_6 - C_{12}$ aliphatic dicarboxylic acids.

19. A flexible basecoat/clearcoat coating composition according to claim 1, wherein said amine-aldehyde crosslinking agent of said basecoat composition is employed in an amount of from about 5 to
5 about 60 weight percent based on the weight of said hydroxy-containing modified polyester present in said basecoat composition.



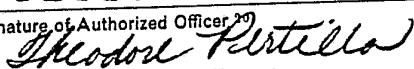
- 30 -

20. A flexible basecoat/clearcoat composition according to claim 1, wherein said hydroxy-containing urethane modified polyester of said basecoat composition has a number average molecular weight ($\overline{M}_n$) of between about
5 2000 and about 4000.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/01604

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. ³ : C08L 61/28 ; C08L 75/06 U.S. 427/409, 412.5; 428/423.3; 525/440, 456; 528/60, 85		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	427/409, 412.5; 428/423.3; 525/440, 456; 528/60, 85.	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
-		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 3,962,522 PUBLISHED 8 JUNE 1976 COLUMN 3, LINE 5-COLUMN 5, LINE 11, EX 1, CHANG ET AL.	1-20
A	US, A, 4,021,505 PUBLISHED 3 MAY 1977 COLUMN 3, LINE 5-COLUMN 4, LINE 62, EX. 1, WANG	1-20
A	US, A, 3,882,189 PUBLISHED 6 MAY 1975 HUDAK	1-20
* Special categories of cited documents: ¹⁵ "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. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ³	
30 NOVEMBER 1983	12 DEC 1983	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 THEODORE PERTILLA	