

United States Patent

Braun

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[45] Aug. 15, 1972

[54] **POLYESTERS WITH SUBSTITUTED AMINE END GROUPS**

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[21] Appl. No.: **120,769**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 776,823, Nov. 18, 1968, abandoned.

[52] U.S. Cl. **260/77**, 252/62.5, 260/37 R, 260/75 TN, 260/77.5 AN, 260/77.5 MA, 260/77.5 AT, 260/78.3 R, 260/482 C, 260/830, 260/835, 260/838, 260/842, 260/849, 260/857

[51] Int. Cl. **C08g 39/10**, C08g 17/14

[58] Field of Search.....260/78.3 R, 482 B, 482 C, 75 TN, 260/77.5 AN, 77.5 MA, 77.5 AT, 77, 77.5 R

[56] **References Cited**

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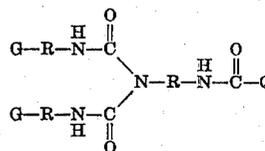
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[57] **ABSTRACT**

Polyesters represented by the general structure



useful as film-formers in coating compositions wherein G may be isocyanate, amino, carbamate, or urea groups, and Q is a dicarboxylic acid - diol or polylactone polyester chain.

3 Claims, No Drawings

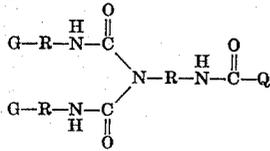
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POLYESTERS WITH SUBSTITUTED AMINE END GROUPS

CROSS-REFERENCE TO RELATED APPLICATIONS

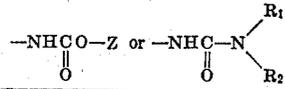
This application is a continuation-in-part of application Ser. No. 776,823, filed Nov. 18, 1968, and now abandoned.

STATEMENT OF THE INVENTION

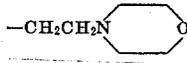
This invention relates to polyesters. It is more particularly directed to polyesters represented by the structure



where G can be -NCO, -NH₂,

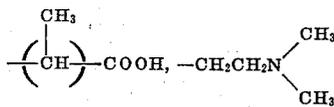


where Z can be alkyl of one through 20 carbon atoms, hydroxyalkyl of one through 20 carbon atoms, carboxyalkyl of one through 20 carbon atoms, hydroxy/carboxy alkyl of one through 20 carbon atoms, alkylene-dialkylamino,



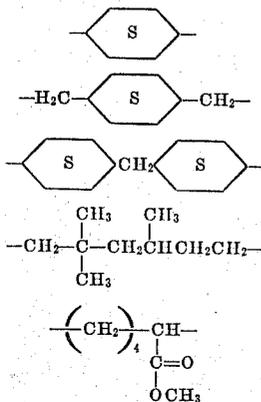
or -CH₂CH₂NHNH₂;
and

R₁ and R₂ can be hydrogen, alkyl of one through six carbon atoms, -NH₂, -O

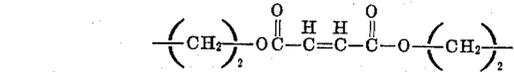
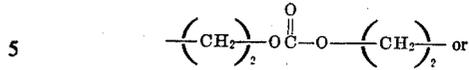
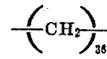


or
-C(=O)-(CH₂)₃

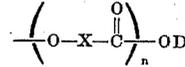
R can be alkylene of two through ten carbon atoms, phenylene, tolylene,



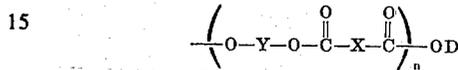
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Q can be



or



where D can be alkyl of one through 18 carbon atoms;
X and Y can be phenylene or alkylene of two through 18 carbon atoms;
and
n is a number 10-500.

UTILITY

The polymers of the invention are useful as film-formers in coating compositions, particularly when combined with a second polymer having complementary reactive groups. Illustrative of such second polymers are heat reactive phenolics, polyglycidyl ethers and esters, polyisocyanate resins, butylated urea/formaldehyde resins and melamine/formaldehyde/alkanol resins.

The polymers of the invention can be cured as film-formers by mixing from about 55 to about 95 parts of the polymer with from about 5 to 45 parts of the second complementary polymer, in a suitable solvent. This solution can then be used directly to give clear coatings or it may be pigmented as desired.

The coating composition can be applied conventionally and is preferably then baked for from about 10 to 30 minutes at 80°-200°C.

The polymers of the invention are also useful as aids for dispersing solid particles in organic liquids. They are especially useful as aids for dispersing pigments in organic liquids. Illustrative of the pigments which can be dispersed are titanium dioxide, carbon black, zinc oxide, lead titanate, potassium titanate, antimony oxide, lithopone, phthalocyanine blue, toluidine red, quinacridone and the like.

Pigment dispersions made with polymers of the invention are remarkably resistant to flocculation, which gives the paints into which dispersions are incorporated higher initial gloss, better hiding and tinting strength, and makes them resistant to color drift and gloss loss. These pigment dispersions can also be used satisfactorily with many more diverse types of paints than conventional pigment dispersions. Moreover, a dispersion made with a polymer of the invention can have a significantly higher pigment content, while retaining the same degree of fluidity, than when conventional aids are used.

The polymers of the invention can be used as pigment dispersing aids by dissolving from 0.001 to about 2.00 grams of polymer per square meter¹ (Measured by the Brunauer, Emmett and Teller nitrogen adsorption method described on page 30 of "Colloidal Disper-

Active hydrogen compound	Resulting G group
$\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$	$-\text{NHCO}(\text{CH}_3)\text{NHCH}(\text{CH}_3)\text{COOH}$
$\text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	$-\text{NHCO}(\text{CH}_3)\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	$-\text{NHCO}(\text{CH}_3)\text{NHCH}_2\text{C}_6\text{H}_5$
$\text{C}_6\text{H}_5\text{NH}_2$	$-\text{NHCO}(\text{CH}_3)\text{NHC}_6\text{H}_5$
$\text{HOCH}_2\text{C}(\text{CH}_2\text{OH})_2\text{CH}_2$	$-\text{NHCO}(\text{CH}_3)\text{OCH}_2\text{C}(\text{CH}_2\text{OH})_2$

To make such a modification, 1-2 moles of reactant for each mole of the polyester-isocyanate product is added to the polyester-isocyanate reaction mass, together with another 0.1% (by weight) of dibutyl tin dilaurate. This mixture is then heated for about one hour at 80°-130°C.

The resulting polymer can be isolated from the reaction mass by heating it at 100°C. for 1 hour at 20 mm. pressure to strip off volatiles.

The physical properties of the polymers of the invention thus prepared range from viscous liquid to friable solid. They are soluble in common organic liquids such as toluene, ethyl acetate, tetrahydrofuran, acetone, hexane, cyclohexane and dimethylformamide.

EXAMPLES

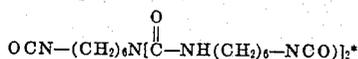
The following examples are submitted so that the invention may be more readily understood and practiced.

Those skilled in the art will no doubt be able to compose numerous variations on their central theme, such as the attachment of innocuous substituents. It is naturally considered that these variations are a part of the invention.

In the Examples all parts are by weight unless otherwise indicated.

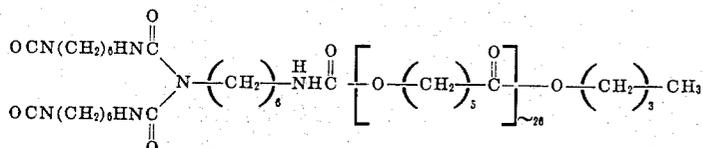
EXAMPLE 1

Fifty-nine and two tenths parts of butyl alcohol initiated polycaprolactone (molecular weight 2960) were dissolved in 100 parts of reagent grade benzene. To this were added, with stirring and in a nitrogen atmosphere, 15.3 parts of a 75 percent solution of



in cellosolve acetate. One-tenth part of dibutyl tin dilaurate catalyst was added and the mixture heated at 80°C. for 1 hour.

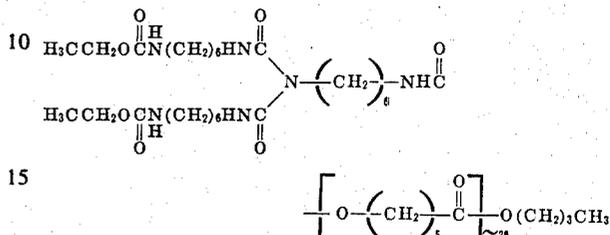
The solvent was stripped off at 100°C. and 20 mm. of pressure to give a waxy solid having the structure



EXAMPLE 2

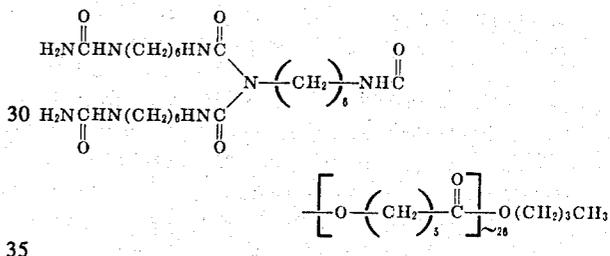
To the product of Example 1, before stripping, were added 5 parts of absolute ethanol and 0.1 part of dibutyl tin dilaurate. This mixture was refluxed for 1 hour.

Solvent was removed by stripping at 100°C. and 20 mm. of pressure. The product was a waxy solid having the structure



EXAMPLE 3

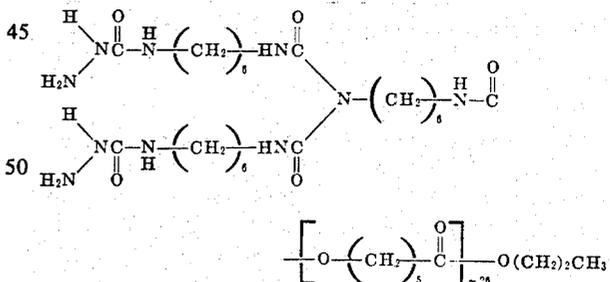
For thirty minutes, ammonia gas was bubbled through the final reaction mass (before stripping) of Example 1. Excess ammonia and solvent were then removed by stripping at 100°C. and 20 mm. of pressure to give a waxy solid having the structure



EXAMPLE 4

To the product of Example 1, before stripping, were added 3.5 parts of anhydrous hydrazine. The mixture was heated at 80°C. for 1 hour.

Excess hydrazine and solvent were removed by stripping at 100°C. and 20 mm. of pressure to give a waxy solid having the structure



EXAMPLE 5

To the product of Example 1, before stripping, were added 3 parts of dimethylol propionic acid and 0.1 part of dibutyl tin dilaurate. The mixture was heated for 1 hour at 80°C.

