Title: AMINE-MODIFIED POLYESTER PIGMENT DISPERSING AGENTS

\[
\begin{align*}
H & \\
H_2N - R_a - N - R_b & (I)
\end{align*}
\]

Abstract

Pigment dispersing agents are disclosed which comprise the reaction product of a polyester having both hydroxyl and carboxylic acid groups with 0.02 to 0.4 millimoles of total amine per gram of polyester, said amine being of formula (I) wherein \(R_a\) is alkylene containing from 2 to 6 carbon atoms and \(R_b\) is hydroxy-substituted alkyl in which the alkyl group contains from 2 to 12 carbon atoms; the percentage by weight being based on total weight of polyester and amine. The pigment dispersing agent has excellent pigment dispersing properties, provides increased color strength and improves the flow and leveling of the pigmented coating. The dispersing agent is particularly useful in pigmented, acid catalyzable coating compositions comprising as the principal film-forming resin an active hydrogen group-containing material and an aminoplast curing agent. The pigment dispersing agents, although containing amine groups, do not adversely affect the cure of such film-forming compositions as can other amine group-containing dispersing agents, and because of the presence of hydroxyl groups, the pigment dispersing agents readily react into the cured film.
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AMINE-MODIFIED POLYESTER PIGMENT DISPERSING AGENTS

Background of the Invention

Field of the Invention: The present invention relates to pigment dispersing agents; to dispersions of pigments containing such dispersing agents; to a method of preparing such dispersions and to coating compositions containing such dispersions.

Brief Description of the Prior Art: Pigmented coating compositions are useful for their aesthetic as well as protective features. The coating compositions contain a film-forming resin and a pigment dispersed in a liquid carrier. It is important that the pigment be satisfactorily dispersed throughout the film which results from the application of the coating composition. Accordingly, the pigment must be well dispersed throughout the liquid coating composition. Normally, the pigment is first dispersed in a pigment dispersing agent. The resulting dispersion is then mixed with the main film-forming resin of the composition and other necessary components to produce the final pigmented coating composition.

A large number of different dispersants have been used in the manufacture of pigmented coating compositions. Many of the dispersants are low molecular weight surfactants. A problem with these materials is their tendency to exude from the painted film after prolonged weathering resulting in an undesirable appearance.

Polymers are also known as dispersing agents. Examples of such polymers are polyesters which have polar groups associated with them such as carboxylic acid and hydroxyl groups which gives them good pigment wetting and dispersing properties. Unfortunately, many of these polymeric pigment dispersing agents provide for poor color strength and often adversely affect the flow and leveling of the pigmented coating compositions which contain the dispersing agents.
Also, the resulting pigment dispersions may have high viscosities which make them very difficult to handle.

Summary of the Invention

In accordance with the present invention, a pigment dispersing agent comprising the reaction product of a polyester having hydroxyl and carboxylic acid groups with from 0.02 to 0.4 millimoles of total amine per gram of polyester, said amine being of the formula:

\[
\begin{align*}
H & \\
H_2N - R_a - N - R_b & 
\end{align*}
\]

wherein \( R_a \) is alkylene containing from 2 to 6 carbon atoms and \( R_b \) is hydroxy-substituted alkyl in which the alkyl group contains from 2 to 12 carbon atoms.

The invention also provides for pigment dispersions comprising finely divided pigment in the dispersing agent described immediately above.

The invention also provides for a method for preparing such pigment dispersions comprising mixing together under high shear conditions a pigment or an aqueous pigment press cake and a dispersing agent so as to intimately disperse the pigment throughout the dispersing agent described above.

The invention also provides for a coating composition which is catalyzed by acid comprising as the principal film-forming resin an active hydrogen-containing material, an aminoplast curing agent, pigment and the pigment dispersing agent described above.

Additional Prior Art

Amine-modified polyesters are known for use as pigment dispersing agents. For example, U.S. 3,882,088 discloses polyesters bearing polyethylenimine terminal groups. The polyesters can be prepared by reacting a hydroxyl group or a carboxylic acid group containing polyester with a compound containing a linking group such as a diisocyanate and further reacting with polyethylenimine to form the polyester bearing terminal polyethylenimine groups.
The pigment grinding vehicles of U.S. 3,882,088 differ from those of the present invention in that they require a linking group to link the polyester with the polyethylenimine, and secondly, compared with the present invention, they have relatively high residual amine contents, i.e., low amine equivalent weights. The presence of high residual amine contents can adversely affect acid catalyzed cures of the main film-forming resin.

U.S. 4,123,422 discloses amide-modified polyester polyols which are formed from reacting a polyester polyol with a primary or secondary amine of the formula:

$$N(H)(R)_{a}(C_yH_{2y}OH)_b$$

where R is hydrogen or an alkyl group containing from 1 to 4 carbon atoms, y is 2 or 3, a is 0 or 1 and b is 1 or 2 with the proviso that $a+b=2$. The amide-modified polyesters are disclosed as being useful as polyol components in two-package urethane coating systems. The reference also discloses that pigment can be incorporated into the polyol package by grinding titanium dioxide pigment into the amide polyester polyol at a ratio of 6:1 on a solids basis, i.e., note Example V.

The amide-modified polyesters of U.S. 4,123,422 differ from the amine-modified polyesters of the present invention in that upon reacting the primary or secondary amine with the polyester polyol, the resultant reaction product of U.S. 4,123,422 does not contain a free secondary amine as does the reaction product of the present invention. It is believed that the secondary amine functionality results in improved pigment dispersing ability compared to the reaction products of U.S. 4,123,422.

U.S. 4,224,212 discloses pigment dispersing agents comprising a poly(lower alkylene)imine chain to which is attached at least two polyester chains by means of salt and/or amide links. The polymer architecture has the polyethylenimine chains internal to the polymer and not as a pendant end group, i.e., two polyester chains are attached to each polyethylenimine group as opposed to the present invention in which the amine group is pendant to the polyester chain. Also, the pigment dispersing agents have relatively high residual amine contents compared with the pigment dispersing agents of the present invention.
U.S. 4,735,984 discloses pigment dispersing agents comprising the reaction product of polyamines having two or more primary amino groups and/or a secondary amino group with at least one polyisocyanate having two or more isocyanate groups.

U.S. 5,000,792 discloses pigment dispersing agents comprising the reaction product of polyesters having a free carboxyl group with an acid value in the range of 10 to 60 with an amine compound of the formula:

$$\text{NH}_2 - \text{R}_1 - \text{N} - \text{R}_2 - \text{NH}_2$$

wherein $\text{R}_1$ and $\text{R}_2$ are alkylene radicals which can be the same or different, each containing from 2 to 6 carbon atoms, and $\text{R}_3$ is a radical of the formula $\text{CH}_3$- or $\text{C}_2\text{H}_5$-, wherein the reaction is conducted in the range of from about 0.8 to 1.0 equivalent molar ratio of amino groups having reactive hydrogens of said amine compound to free carboxylic acid groups of the polyester.

Once again, the polymer architecture of this particular pigment dispersing agent is considerably different than that of the present invention. In U.S. 5,000,792, the amine compound links together two polyester chains as opposed to the present invention in which the amine is pendant to the polyester chain.

**Detailed Description**

The polyesters which are used in making the pigment dispersing agents of the present invention are produced by reacting a polyhydric alcohol component with a polybasic carboxylic acid component to obtain a polyester containing carboxylic acid groups.

The polyhydric alcohols have a functionality of at least two and contain from 2 to 16 carbon atoms, preferably 2 to 8 carbon atoms. Such polyhydric alcohols include diols, triols and higher polyols. Useful diols include alkylene glycols, e.g., ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol and cyclohexanediol. Triols and higher polyols include trimethylolethane, trimethylolpropane,
glycerol, 1,2,6-hexanetriol and pentaerythritol. Mixtures of polyhydric alcohols can also be used.

The polybasic carboxylic acid has a functionality of at least two and can contain from 4 to 36 carbon atoms. It can be an aliphatic carboxylic acid, an alicyclic acid or an aromatic carboxylic acid, providing it has the required number of carbon atoms and proper degree of functionality. For purposes of the present invention, the aromatic nuclei of aromatic carboxylic acids, for example, phthalic acid, are regarded as saturated since the double bonds are relatively unreactive. (This is as opposed to the reactivity of an alpha-beta unsaturated acid, for example, fumaric acid.) Therefore, wherever the term "saturated polyester polyol" is utilized, it is understood that this term includes a compound containing aromatic unsaturation.

Examples of polybasic carboxylic acids useful herein include phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, hexahydrophthalic anhydride, succinic acid, succinic anhydride, glutaric acid, adipic acid, azelaic acid, sebamic acid, dimerized fatty acids and mixtures thereof. The aliphatic carboxylic acids can contain from 4 to 36 carbon atoms while the alicyclic or aromatic carboxylic acids contain from 6 to 14 carbon atoms (inclusive of the number of carbon atoms in the carboxyl group). The dicarboxylic acids are the preferred polybasic carboxylic acids, although minor amounts of more higher functional carboxylic acids, for example, trimellitic acid, can be included with the dicarboxylic acid.

The carboxylic acid group-containing polyester is produced using conventional batch or continuous processing techniques with the reaction conditions and ratio of reactants being chosen so as to provide a product having the desired hydroxyl and carboxyl groups. The polyester should have an acid number of from about 0.1 to 30 and preferably from about 5 to 15 (on a solids basis). Acid values less than 0.1 are undesirable because of the difficulty in dispersing basic pigments, whereas acid values greater than 30 are undesirable because of paste instability and high paste viscosities.

The hydroxyl value of the polyester is typically at least 20, preferably within the range of 50 to 300 (on a solids basis). Lower hydroxyl values provide insufficient reactive sites for curing.
The polyester preferably will have a weight average molecular weight (Mw) of 500 to 100,000, more preferably 800 to 40,000. Molecular weights less than 500 are undesirable because of paste instability, whereas molecular weights greater than 100,000 are undesirable because of high paste viscosities. The molecular weights are determined by gel permeation chromatography using a polystyrene standard. Therefore, what is obtained is a polystyrene number. However, for the purpose of the present invention, they are considered molecular weights.

The amine which is reacted with the carboxylic acid group-containing polyester is of the formula:

\[ \text{H} \]

\[ \text{H}_2\text{N} - \text{R}_a - \text{N} - \text{R}_b \]

wherein \( \text{R}_a \) is alkylene containing from 2 to 6 carbon atoms and \( \text{R}_b \) is hydroxy-substituted alkyl in which the alkyl group contains from 2 to 12 carbon atoms. Preferably, \( \text{R}_a \) is ethylene and \( \text{R}_b \) is hydroxyethyl. Examples of suitable amines include \( \text{N}-\text{aminoethylethanolamine} \), \( \text{N}-\text{aminopropylethanolamine} \), \( \text{N}-\text{aminoethylhydroxypropylamine} \) and \( \text{N}-\text{aminoethylhydroxyethylamine} \).

The amount of amine which is reacted with the polyester is from about 0.02 to 0.4, preferably 0.03 to 0.3 millimoles of total amine per gram of polyester. Amounts less than 0.02 millimoles per gram of polyester are undesirable because the resulting pigment dispersing agent will not have sufficient pigment dispersing properties, whereas amounts greater than 0.4 millimoles per gram of polyester are undesirable because the higher amine contents inhibit acid catalyzed cure, such as an aminoplast cure, when the pigment dispersing agent is incorporated into such curable coating compositions.

The equivalent ratio of amine (i.e., equivalents of primary amine group) to carboxylic acid in the polyester is usually from about 0.05 to 1:1. Controlling the equivalent ratio in this manner insures that the resultant pigment dispersing agent will have groups of the structure:
5 pendant to the polyester chain backbone. Having these pendant groups
with both secondary amino and hydroxyl functionality results in very
effective pigment dispersing qualities.

The reaction of the amine with the polyester is typically
conducted by heating the polyester to a temperature of about 120° to
170°C. and then adding the amine and holding at a temperature of 120°
to 170°C., while removing any water that is formed as the reaction
proceeds.

To form a pigment dispersion, the solid pigment, pigment
dispersing agent and optionally organic solvent are mixed in any
order and the mixture then subjected to high shear mixing conditions
to finely divide and to intimately disperse the pigment throughout
the dispersing agent. Examples of high shear mixing are steel ball,
sand or zirconia medium milling. Typically, the pigment will have a
particle size of about 0.1 to 10 microns and the pigment dispersion
will contain a pigment to resin weight ratio in the range of from
about 0.01 to 10:1.

The pigment can be an inorganic or organic compound which is
substantially insoluble in the medium in which it is incorporated
which is capable of comminution into a finely divided form. Examples
of suitable pigments include iron oxide, lead oxide, strontium
chromate, carbon black, coal dust, titanium dioxide, talc, barium
sulfate, as well as the color pigments such as cadmium yellow,
cadmium red, chromium yellow, phthalo cyanine blue, toluidine red, and
the quinacridone pigments.

Examples of organic solvents which may be used with the
dispersing agents include aromatic hydrocarbons such as toluene and
xylene; ketones such as methyl ethyl ketone and methyl isobutyl
ketone; esters such as butyl acetate, 2-ethoxyethyl acetate and
2-butoxyethyl acetate; and glycol ethers such as propylene glycol
monomethyl ether. When organic solvents are present in the pigment
dispersion, they are typically present in amounts of about 10 to 40
percent by weight based on weight of pigment dispersion.
The pigment dispersing agents of the present invention can also be used to disperse pigment by a flushing mechanism wherein the dispersing agent is used to displace water in an aqueous pigment press cake and to intimately disperse the pigment in the dispersing agent by mixing the dispersing agent with the press cake under high shear conditions such as with a Sigma Blade mixer. Typically, the resulting pigment dispersion will contain a pigment to resin weight ratio in the range of from about 0.01 to 10:1 depending somewhat on the pigment used and its surface area.

The pigment dispersions of the present invention are particularly useful in pigmented, acid catalyzable coating compositions, for example, coating compositions comprising as the principal film-forming resin an active hydrogen group-containing material and an aminoplast curing agent.

The term "active hydrogen" refers to hydrogens which, because of their position in the polymer molecule, display reactivity with the aminoplast. Examples of active hydrogens include hydrogen atoms attached to oxygen and specific examples include hydroxyl and carboxylic acid, which are the most preferred. Examples of suitable active hydrogen-containing polymers are acrylic polymers containing hydroxyl groups, and polyester polyols including hydroxyl group-containing alkyds. Also, polyurethane polyols can be used. Typically, these polymers will have hydroxyl values of from about 20 to 200 (on a solids basis).

Aminoplast curing agents are aldehyde condensation products of amines or amides with aldehydes. Examples of suitable amines or amides are melamine, benzoguanamine and urea. Generally, the aldehyde employed is formaldehyde, although products can be made from other aldehydes such as acetaldehyde and furfuryl. The condensation products contain methylole or similar alkylol groups depending upon the particular aldehyde employed. Preferably, these alkylol groups are etherified by reaction with an alcohol such as one which contains 1 to 4 carbon atoms such as methanol or butanol. Aminoplasts are commercially available from American Cyanamid Company under the trademark CYMEL and from Monsanto Chemical Company under the trademark RESIMINE.
Such compositions cure in an acidic environment and to promote curing, the compositions usually contain an acid catalyst such as an acidic material, for example, an acid phosphate such as phenyl acid phosphate, and a sulfonic acid such as paratoluene 5 sulfonic acid.

The coating compositions will typically contain from 45 to 80 percent by weight of the active hydrogen-containing polymer, from 20 to 55 percent by weight of the aminoplast curing agent, the percentages by weight being based on total weight of active hydrogen-containing polymer and aminoplast curing agent. With regard to the other ingredients in the coating composition, the acid catalyst is present in amounts of up to 5 percent by weight and the pigment dispersing agent is present in amounts of 1 to 70 percent by weight; the percentages by weight being based on weight of resin solids in the coating composition. The pigment is typically present in the composition in amounts of about 0.1 to 85 percent by weight based on total solids of the coating composition.

The coating compositions will usually contain an organic solvent and/or diluent. Examples of such solvents or diluents would include those mentioned above in connection with the preparation of the pigment paste. Typically, the solvent would be present in amounts of about 30 to 70 percent by weight based on total weight of the coating composition.

The coating composition can additionally contain optional materials well known in the art for protective and decorative coating compositions. Examples would be UV light stabilizers or UV light absorbers in the event that the coating is designed for exterior applications. Examples of other optional coating ingredients would be fillers, plasticizers, reactive diluents, anti-oxidants, flow control agents and other formulating additives. These optional materials generally constitute up to 30 percent by weight of the coating composition based on total weight of resin solids in the coating composition.

The following examples are illustrative of the invention. All percentages are on a weight basis unless otherwise indicated. All acid values and hydroxyl values are on a solids basis unless otherwise indicated.
The Examples show the preparation of various pigment dispersing agents and pigment dispersions in accordance with the practice of the invention and the formulation of coating compositions with the pigment dispersions. For the purpose of comparison, a pigment dispersion was prepared with an amide-modified polyester polyol as generally taught in U.S. 4,123,422, formulated into a paint and its color strength compared to a paint obtained using the pigment dispersions of the present invention. Also for the purpose of comparison, a pigment dispersion was prepared with a pigment dispersing agent as generally described in U.S. 4,735,984 and formulated into an acid catalyzable paint and the cure response of the paint compared to a paint obtained using the pigment dispersion of the present invention.

EXAMPLES

The following Examples I-III show the preparation of various pigment dispersing agents in accordance with the present invention.

Example I

A flask was charged with 128 grams (g) water, 1157 g neopentyl glycol, 1022 g hydroxy pivalyl hydroxy pivalate, 510 g trimethylol propane, 480 g adipic acid, 2160 g isophthalic acid and 9.4 g dibutyltin oxide. A nitrogen blanket was maintained on the mixture which was heated to 210°C. and held at this temperature until the acid value was reduced to 11-15 units. The mixture was then cooled to 150°C. and 65 g xylene was added, followed by 1221 g of caprolactone over 1 hour. The resulting mixture was held at 150°C. until a constant viscosity was reached. To this was added 260 g xylene, 35 g amino ethyl ethanolamine and 3 g butyl stannic acid. The reaction was held at 150°C. until 6 g of water was removed by azeotropic distillation. After dilution with xylene, the final properties of the pigment dispersing agent were:

Solids 68.8%
Gardner-Holdt Viscosity W-
Acid value 5.7
Hydroxyl value 73.3
Mw = 6874
Example II

A flask was charged with 76 g water, 701 g neopentyl glycol, 463 g trimethylolpropane, 698 g sebacic acid, 860 g isophthalic acid and 1 g butylstannonic acid. A nitrogen blanket was maintained and the mixture was heated to 220°C. and held at this temperature until the acid value was reduced to 6-10 units. The mixture was cooled to 150°C. and 148 g xylene and 19.6 g of aminoethylethanolamine added. The reaction was held at 150°C. until 4 g of water was removed by azeotropic distillation. After dilution with butyl acetate, the final properties of the pigment dispersing agent were:

- Solids 60.8%
- Gardner-Holdt Viscosity T-
- Acid value 4.1
- Hydroxyl value 145
- $M_w = 42712$

Example III

A flask was charged with 5452 g of trimethylpentanediol, 1481 g adipic acid, 2063 g isophthalic acid and 3.2 g of dibutyltin oxide. A nitrogen blanket was maintained and the mixture was heated to 205°C. and held at this temperature until the acid value was reduced to 8-10 units. The mixture was cooled to 150°C. and 476 g xylene, 49.5 g aminoethylethanolamine and 3.6 g of butylstannonic acid added. The reaction was held at 150°C. with 9 g of water being removed by azeotropic distillation. After dilution with xylene, the final properties were:

- Solids 81.2%
- Gardner-Holdt Viscosity Z3+
- Acid value 6.1
- Hydroxyl value 184
- $M_w = 1259$

The following Examples IV and V show the preparation of pigment dispersions using the pigment dispersing agents of Examples I and II and the formulation of paints from the resulting pigment dispersions.
Example IV

To 128 g of the pigment dispersing agent of Example I was added 80 g of 2-butoxyethyl acetate. To this solution was added with agitation 57 g of TiO₂, 1.5 g carbon black, 18 g iron oxide, 7 g of strontium chromate pigment and 343 g of barytes. This composition was then ground on a sand mill to an 8.0 hegman. To form the final paint, 652 g of the above pigment dispersion was let down with the following mixture:

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<tr>
<th>Ingredient</th>
<th>Weight in Grams</th>
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<tr>
<td>Amine-modified polyester used in Example 1</td>
<td>238</td>
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<tr>
<td>68% Solids polyester composed of trimethylolpropane/ethanol/methylhexahydrophthalic anhydride (19/9/72 weight ratio) in methyl isobutyl ketone, Mw = 500, acid value = 180 measured on solution</td>
<td>28</td>
</tr>
<tr>
<td>CYMEL 1158 (butylated melamine/formaldehyde condensate from American Cyanamid)</td>
<td>140</td>
</tr>
<tr>
<td>BEETLE 80 (butylated urea formaldehyde resin from American Cyanamid)</td>
<td>12</td>
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<tr>
<td>Methylamyl ketone</td>
<td>33</td>
</tr>
<tr>
<td>2-Butoxyethyl acetate</td>
<td>29</td>
</tr>
<tr>
<td>Propyl alcohol</td>
<td>29</td>
</tr>
</tbody>
</table>

The final properties of the paint were:

Total solids = 71.0%
Total Pigment to Binder Ratio = 1.07

The resulting paint when coated onto a substrate cured well at elevated temperature and the pigment dispersing agent was constructed such that it became an integral part of the crosslinked film. It was observed that the above paint had lower thixotropy, better wetting, gloss, flow and lower viscosity than a similar paint which was formulated with a polyester dispersing agent which was not amine modified.

Example V

The pigment dispersing agent of Example II was formulated into a paint as follows: To 154 g of the pigment dispersing agent
was added 36 g of isobutyl acetate and 36 g of monomethyl ether propylene glycol acetate. To this solution was added with agitation 25 g of carbon black pigment. The resulting slurry was stirred via Cowles blade for 5 minutes, then poured into an Eiger mill filled 5 with steel shot and ground for 12 passes. The final paint was obtained by letting down 100 g of the above pigment dispersion with 586 g of the following mixture:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percent by Weight</th>
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<tbody>
<tr>
<td>90% Solids polyester of trimethylpentane diol and hexahydrophthalic anhydride (65/35 weight ratio) in methyl isobutyl ketone, (acid value = 8, OH value = 211 measured on solution)</td>
<td>15.4</td>
</tr>
<tr>
<td>71% Solids polyurethane obtained from diethylene glycol, dimethylolpropionic acid, isophorone diisocyanate and caprolactone (10.5/0.9/13/76 weight ratio) in monomethyl ether propylene glycol acetate and methyl isobutyl ketone (78/22 weight ratio); Mw = 35,000, OH value = 40 measured on solution</td>
<td>15.9</td>
</tr>
<tr>
<td>50% Solids polyurethane obtained from diethylene glycol, dimethylolpropionic acid, 4,4'-diphenylmethane diisocyanate, ethanolamine and caprolactone (6/3.1/18.8/0.2/71.4 weight ratio) in butanol, isopropyl alcohol, methyl isobutyl ketone and methyl ethyl ketone (4/9/36/51 weight ratio), Mw = 30,000, OH value = 92 measured on solution</td>
<td>5.6</td>
</tr>
<tr>
<td>Flow control agent (prepared in accordance with Example II of U.S. Patent No. 4,147,688 and diluted on a 1:1 volume basis with 2-hexoxyethanol</td>
<td>2.5</td>
</tr>
<tr>
<td>CYMEL 1130 (methylated, butylated melamine/formaldehyde from American Cyanamid)</td>
<td>19.5</td>
</tr>
<tr>
<td>Ultraviolet light absorbers</td>
<td>1.1</td>
</tr>
<tr>
<td>n-amyl alcohol</td>
<td>5.9</td>
</tr>
<tr>
<td>Monomethyl ether propylene glycol acetate</td>
<td>10.1</td>
</tr>
<tr>
<td>Isobutyl acetate</td>
<td>8.3</td>
</tr>
</tbody>
</table>
The final properties of the paint were:

Total solids = 41.6%

Total Pigment to Resin Ratio = 0.19

The resulting paint when coated on a substrate cured well at elevated 5 temperature (30 minutes at 250°F. (121°C.)) and the pigment dispersing agent was constructed such that it became an integral part of the crosslinked film. Paints employing the current invention had better color development, transparency, better flow and leveling and lower viscosity than similar paints in which the paint was formulated 10 with a polyester dispersing agent which was not amine modified.

Comparative Example VI

For the purpose of comparison, a paint was prepared using as the pigment dispersing agent the amide-modified polyester generally described in U.S. 4,123,422.

A flask was charged with 27 g water, 251 g neopentyl glycol, 165 g trimethylolpropane, 249 g sebacic acid, 307 g isophthalic acid and 0.35 g butylstannoic acid. A nitrogen blanket was maintained and the mixture was heated to 220°C. and held at this temperature until the acid value was reduced to 6-10 units. The mixture was cooled to 150°C. and 53 g xylene, and 6.3 g of diethanolamine added. The reaction was held at 150°C. while removing water by azeotropic distillation. After dilution with butyl acetate, the final properties of the pigment dispersing agent were:

- Solids 60.9%
- Gardner-Holdt Viscosity V-
- Acid value 4.1
- Hydroxyl value 135.4
- Mw = 23568

A pigment dispersion and paint were prepared with the above-described amine-modified polyester as the pigment dispersing agent by the procedure generally described in Example V. When the paint was coated onto a substrate and cured, the resulting cured coating was poorer in color development (black jetness), had lower gloss and was hazier than the cured coating of Example V.
Comparative Example VII

For the purpose of comparison, a paint was prepared using a pigment dispersing agent as generally described in U.S. 4,735,984.

A flask was charged with 27 g water, 251 g neopentyl glycol, 165 g trimethylolpropane, 249 g sebacic acid, 307 g isophthalic acid and 0.35 g butylstannoic acid. A nitrogen blanket was maintained and the mixture was heated to 220°C. and held at this temperature until the acid value was reduced to 6-10 units. The solution was cooled to 50°C. and 251 g of propylene glycol monomethyl ether was then added, followed by 4 g of tetraethylpentamine. After 10 minutes, 14.4 g of the isocyanate of 1,6-hexamethylene diisocyanate was added and the solution was stirred until the isocyanate was no longer observed by infrared analysis. After dilution with propylene glycol monomethyl ether, the final properties of the pigment dispersing agent were:

Solids 61.2%  
Gardner-Holdt Viscosity V  
Acid value 8.3  
Mw = 13515

When this material was formulated into a black paint generally as per Example V and the paint applied as a coating and cured, the resulting cured coating had inferior solvent resistance and was poorer in color development (black jetness) compared to the cured coating of Example V.

Example VIII

The following example shows the preparation of a pigment dispersing agent and the use of the dispersing agent to form a pigment dispersion by a flushing technique. The pigment dispersing agent was prepared as follows:

A flask was charged with 2351 g of dimer fatty acid (EMPOL 1008 from Henkel Corp.), 256 g trimethylolpropane, 661 g neopentyl glycol, 697 g cyclohexanediethanol, 0.8 g butylstannoic acid and 2 g triphenylphosphite. A nitrogen blanket was maintained and the mixture was heated to 180°C. and held at this temperature until the acid value was reduced to 7-10 units. The mixture was cooled to 150°C. and to this was added 202 g xylene and 21 g of
aminoethylethanolamine. The reaction was held at 150°C. until 4 g of
water was removed by azeotropic distillation. The final properties
of the pigment dispersing agent were:

Solids 80.5%
Gardner-Holdt Viscosity Z2-
Acid value 5.6
Hydroxyl value 302
Mw = 1663

The pigment dispersing agent was formulated into a pigment
dispersion by flushing as follows: To 300 g of a 32 percent solids
quinacridone magenta press cake (Sun Chemical) was added with
agitation in a double Sigma Blade mixer 136 g of the pigment
dispersing agent. After mixing for about 10 minutes, another 240 g
of press cake was added, followed by mixing for about 10 minutes and
the addition of 80 g of the pigment dispersing agent. Mixing was
continued for about 5 minutes followed by the addition of two 90 g
aliquots of press cake. Agitation was continued for about an
additional 10 minutes to remove the water and intimately disperse the
pigment throughout the dispersing agent.
CLAIMS:

1. A pigment dispersing agent comprising the reaction product of a polyester having hydroxyl and carboxylic acid groups with from 0.02 to 0.4 millimoles of total amine per gram of polyester, said amine being of the formula:

\[
\begin{align*}
H \\
H_2N - R_a - N - R_b
\end{align*}
\]

wherein \( R_a \) is alkylene containing from 2 to 6 carbon atoms and \( R_b \) is hydroxy-substituted alkyl in which the alkyl group contains from 2 to 12 carbon atoms.

2. The pigment dispersing agent of claim 1 in which the polyester has a weight average molecular weight of 500 to 100,000.

3. The pigment dispersing agent of claim 1 in which the polyester has an acid value of 0.1 to 30.

4. The pigment dispersing agent of claim 1 in which the equivalent ratio of primary amine in the amine compound to carboxylic acid in the polyester is from 0.05 to 1:1.

5. The pigment dispersing agent of claim 1 in which \( R_a \) is ethylene.

6. The pigment dispersing agent of claim 1 in which \( R_b \) is hydroxyethyl.

7. The pigment dispersing agent of claim 1 in which the polyester is formed by reacting a polyhydric alcohol component with a polycarboxylic acid component in which the polycarboxylic acid component contains a dimerized fatty acid.

8. A pigment dispersion comprising finely divided pigment dispersed in a dispersing agent characterized in that the dispersing agent is that of claim 1.
9. The pigment dispersion of claim 8 in which the pigment to resin weight ratio is from 0.01 to 10:1.

10. A method for preparing a pigment dispersion comprising mixing together under high shear conditions a pigment and a dispersing agent so as to finely divide and to disperse the pigment throughout the dispersing agent, characterized in that the dispersing agent is that of claim 1.

11. A method for preparing a pigment dispersion comprising mixing together an aqueous pigment press cake with a dispersing agent under high shear conditions so as to displace water and intimately disperse the pigment in the dispersing agent, the improvement characterized in that the dispersing agent is that of claim 7.

12. The method of claim 10 in which the pigment to resin weight ratio is from 0.01 to 10:1.

13. In an acid catalyzable coating composition comprising as the principal film-forming resin an active hydrogen group-containing material, an aminoplast curing agent, pigment and a pigment dispersing agent, characterized in that the pigment dispersing agent is that according to claim 1.

14. The coating composition of claim 13 in which the pigment dispersing agent is present in amounts of 1 to 70 percent by weight based on weight of resin solids.

15. The coating composition of Claim 13 in which the pigment is present in an amount of 0.1 to 85 percent by weight based on total solids of the coating composition.
AMENDED CLAIMS

[received by the International Bureau on 10 December 1992 (10.12.92); original claims 1-9 deleted; original claims 10-15 replaced by amended claims 1-16 (2 pages)]

1. A method for preparing a pigment dispersion comprising mixing together an aqueous pigment press cake with a dispersing agent under high shear conditions so as to displace water and intimately disperse the pigment in the dispersing agent, the improvement characterized in that the dispersing agent comprises the reaction product of a polyester formed from reacting a polyhydric alcohol component with a polycarboxylic acid component, said polyester having hydroxyl and carboxylic acid groups with from 0.02 to 0.4 millimoles of total amine per gram of polyester, said amine being of the formula:

\[
\begin{align*}
  & \text{H} \\
  & \text{H}_2\text{N} - \text{R}_a - \text{N} - \text{R}_b
\end{align*}
\]

wherein \( R_a \) is alkylene containing from 2 to 6 carbon atoms and \( R_b \) is hydroxy-substituted alkyl in which the alkyl group contains from 2 to 12 carbon atoms.

2. The method of claim 1 in which the pigment to resin weight ratio is from 0.01 to 10:1.

3. The method of Claim 1 in which the polyester has a weight average molecular weight of 500 to 100,000.

4. The method of Claim 1 in which the polyester has an acid value of 0.1 to 30.

5. The method of Claim 1 in which the equivalent ratio of primary amine in the amine compound to the carboxylic acid in the polyester is from 0.05 to 1:1.

6. The method of Claim 1 in which \( R_a \) is ethylene.

7. The method of Claim 1 in which \( R_b \) is hydroxyethyl.

8. The method of Claim 1 in which the polycarboxylic acid component contains a dimerized fatty acid.
9. In an acid catalyzable coating composition comprising as the principal film-forming resin an active hydrogen group-containing material, an aminoplast curing agent, pigment and a pigment dispersing agent, characterized in that the pigment dispersing agent comprises the reaction product of a polyester having hydroxyl and carboxylic acid groups with from 0.02 to 0.4 millimoles of total amine per gram of polyester, said amine being of the formula:

\[
\text{H} \\
\text{H}_2\text{N} - \text{R}_a - \text{N} - \text{R}_b
\]

wherein \( \text{R}_a \) is alkylene containing from 2 to 6 carbon atoms and \( \text{R}_b \) is hydroxy-substituted alkyl in which the alkyl group contains from 2 to 12 carbon atoms.

10. The coating composition of claim 9 in which the pigment dispersing agent is present in amounts of 1 to 70 percent by weight based on weight of resin solids.

11. The coating composition of Claim 9 in which the pigment is present in an amount of 0.1 to 85 percent by weight based on total solids of the coating composition.

12. The coating composition of Claim 9 in which the polyester has a weight average molecular weight of 500 to 100,000.

13. The coating composition of Claim 9 in which the polyester has an acid value of 0.1 to 30.

14. The coating composition of Claim 9 in which the equivalent ratio of primary amine in the amine compound to carboxylic acid in the polyester is from 0.05 to 1:1.

15. The coating composition of Claim 9 in which \( \text{R}_a \) is ethylene.

16. The coating composition of Claim 9 in which \( \text{R}_b \) is hydroxyethyl.
Statement Under Article 19.

Enclosed herewith are replacements for pages 17 and 18 of the subject application in which amendments to the claims have been made. The difference between the claims as filed and the claims as amended is as follows.

Claims 1-9 have essentially been cancelled. Original method claims 10-12 now appear as new claims 1-8. Coating composition claims 13-15 have been rewritten as new claims 9-16.

One reference, U.S. 3,882,088 to Thompson, has been cited as being particularly pertinent. This reference discloses that polyesters can be modified with ethylenimines, such as polyethylenimines, to incorporate pendent polyethylenimine groups into the polyester resin molecule. The reference further discloses that the imine modified polyesters are useful as film-formers and coating compositions, particularly combined with a second polymer having complementary reactive groups such as heat reactive phenolics, polyglycidyl ethers and esters, polyisocyanate resins, butylated urea-formaldehyde resins and melamine-formaldehyde-alkanol resins.

Also, it is mentioned in the reference that the polymers disclosed therein are useful as pigment dispersing agents in organic liquids. When used in this manner the polyethylenimine-modified polyesters are added to an organic liquid and then an appropriate amount of pigment is added to the solution, which is then subjected to shear, such as by sand grinding or ball-milling, to deagglomerate and disperse the pigment. The pigment dispersion is then added to the film-forming resin to form a paint.
With regard to the method claims of the present invention, i.e., claims 1-8, these claims specifically relate to a method of preparing a pigment dispersion which comprises mixing together an aqueous pigment press cake with the particularly claimed dispersing agent under high shear conditions so as to displace water and intimately disperse the pigment in the dispersing agent. This process is exemplified in Example VIII of the application. The Thompson reference, on the other hand, does not disclose this method. As mentioned above, the pigment dispersing agents in Thompson are added to organic liquids, followed by the addition of pigment and subjecting the resultant solution to shear by sand grinding or ball-milling. There is no suggestion in Thompson that his polymers would be useful in preparing a pigment dispersion as set forth by the present method claims 1-8.

Regarding claims 9-16, these claims specifically read on an acid catalyzable coating composition comprising, as a principal film-forming resin active hydrogen group-containing materials, aminoplast curing agents, pigments and pigment dispersing agents in which the pigment dispersing agent is as particularly claimed. The Thompson reference simply does not disclose that the polyethylenimine-modified polyesters, when used as pigment dispersing agents, can be used with acid catalyzable coating compositions comprising active hydrogen-containing polymers and aminoplast curing agents. Although Thompson does disclose that his polyethylenimine-modified polyesters can be used in combination with butylated urea-formaldehyde resins and melamine-formaldehyde-alkanol resins, when used in this manner, they are used as the principal film-formers rather than as pigment dispersing agents as specifically required by claims 9-16. This is a significant difference in that applicant has found, as mentioned in the specification on page 6, lines 22-32, that amino-functional pigment dispersing agents can adversely affect the cure of acid catalyzable aminoplast-curable compositions. Therefore, it is necessary to carefully control the residual amine content of the pigment dispersing agent in the manner specifically set forth in the present claims. Thompson, on the other hand, offers no teaching to one skilled in the art of a possible adverse effect of amino-functional pigment dispersing agents with acid catalyzable aminoplast-curable coating compositions.
### A. CLASSIFICATION OF SUBJECT MATTER

<table>
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<th>US CL</th>
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<td>008K 5/10, 5/17</td>
<td>10C/499;525/415,417,437</td>
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### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

| U.S. | 106/499;525/415,417,437 |

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>X</td>
<td>US.A, 3,882,088 (Thompson) 06 May 1975 see col. 1, lines 15-44, 53-57; col. 2, lines 6-16, 39-40,54; col. 4, lines 26-32, col. 6, lines 31-32.</td>
<td>1-15</td>
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<td>A</td>
<td>US.A, 4,123,422 (Eriksen et al.) 31 October 1978 see entire document in general.</td>
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<td>A</td>
<td>US.A, 4,224,212 (Topham) 23 August 1980. See entire document in general.</td>
<td>1-15</td>
</tr>
<tr>
<td>A</td>
<td>US.A, 4,735,984 (Gouji et al.) 5 April 1988. See entire document general.</td>
<td>1-15</td>
</tr>
<tr>
<td>A</td>
<td>US.A, 5,000,792 (Ohata et al.) 19 March 1991. See entire document in general.</td>
<td>1-15</td>
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</table>

Further documents are listed in the continuation of Box C. See patent family annex.

- "A" Special category of cited documents:
  - "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
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Date of the actual completion of the international search: 07 AUGUST 1992

Date of mailing of the international search report: 26 OCT 1992

Name and mailing address of the ISA/ Commissioner of Patents and Trademarks

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