A resin cleaner composition is provided herein for use as a cleaning solvent to remove cured, partially cured and uncured polyester or vinyl ester resin containing a free radical polymerization initiator from resin fabrication tools. The composition is characterized by the presence therein of a free radical inhibitor which suppresses the rate of free radical polymerization.
(54) Title: RESIN CLEANER COMPOSITION

(57) Abstract

A resin cleaner composition is provided herein for use as a cleaning solvent to remove cured, partially cured and uncured polyester or vinyl ester resin containing a free radical polymerization initiator from resin fabrication tools. The composition is characterized by the presence therein of a free radical inhibitor which suppresses the rate of free radical polymerization.
This invention relates to a resin cleaner composition for use in the fiberglass fabrication industry, and, more particularly, to a solvent composition which achieves an increased resin loading in the solvent without increasing its rate of polymerization.

Traditionally, companies which use fiberglass in the manufacture of boats, automobile parts, tanks, panels and the like have used acetone as a clean-up solvent. While acetone is a very effective solvent for uncured fiberglass, i.e. unsaturated polyester or vinyl ester resins containing polymerization initiators, it is a highly volatile, low flash point, material which is considered hazardous and flammable. Furthermore, the loading of uncured fiberglass in acetone is limited by the rate of polymerization or gellation of the uncured resin in acetone solution. Accordingly, after a short period of use, the resin solution must be discarded and fresh solvent used.

An improved substitute for acetone for this use is available in the form of N-methylpyrrolidone (M-Pyrol®) or NMP, which is an excellent solvent for fiberglass resins, much less volatile than acetone, biodegradable, substantially less toxic, and which exhibits loading characteristics at least comparable to that displayed by acetone. However, the art has desired a resin cleaner composition having the advantageous properties of NMP with increased fiberglass loading properties during use.
A resin cleaner composition is provided herein for use as a cleaning solvent to remove cured, partially cured and uncured polyester or vinyl ester resin containing a free radical polymerization initiator from fiberglass fabrication tools. The composition is characterized by the presence therein of a free radical inhibitor which suppresses the rate of free radical polymerization. Thereby the resin can be loaded in increased amounts in the composition without an accompanying increase in polymerization of the resin.

In the preferred form of the invention, the inhibitor is a substituted phenol, e.g. vanillin, 4-t-butylcatechol, hydroquinone, butylated hydroxytoluene and the like, and the solvent is NMP, optionally including a diluent such as a dibasic acid ester (DBE), such as dimethyl adipate, dimethyl glutarate, dimethyl succinate, \( \gamma \)-butyrolactone (BLO), tetrahydrofurfuryl alcohol, propylene glycol ethers, propylene carbonate, dimethyl imidazolidinone, tetramethyl urea, terpenes, and mixtures thereof. The substituted phenol inhibitor suitably is present in the amount of at least about 0.005\% by weight of the composition, preferably about 0.01-0.03\%, and optimally, about 0.02\%. 
The resin cleaner composition of the invention comprises:

<table>
<thead>
<tr>
<th>Essential Components</th>
<th>Suitable</th>
<th>Preferred</th>
<th>Optimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>5-99.9</td>
<td>30-70</td>
<td>49.7</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>at least 0.005</td>
<td>0.01-0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>e.g. substituted phenol</td>
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<td></td>
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</table>

Optional Components

| Diluent          | 0-95 | 30-70 | 49.7 |
| e.g. BLO or DBE |      |       |      |

| Surfactant       | 0-1.5 | 0.2-1.0 | 0.5 |
| e.g. Emulphogene® DA 630 | |      | |

| Odor masking agent | 0-0.2 | 0.05-0.15 | 0.1 |
| e.g. Arylene® T  |      |           |     |

The solvent and diluent in the composition of the invention perform the desired role of effectively removing the cured, partially cured and uncured polyester or vinyl ester resin from the work tools used in the fiberglass fabrication industry. The inhibitor material therein functions to interfere with free radical polymerization of catalyzed resin to reduce the rate of polymerization or gelation of the uncured resin in the solvent. In use the composition thus increases the uncured resin loading factor in the composition.
A typically free radical initiator used to cure the resin composition is methyl ethyl ketone peroxide, although other free radical initiators known in the art may be employed.

The inhibitor used in this invention to suppress or interfere with free radical polymerization suitably is soluble in the solvent composition and is effective in a reasonably small amount. Substituted phenols are preferred inhibitors for this purpose. Preferred substituted phenols include such compounds as vanillin, butyl catechol, hydroquinone and butylated hydroxy toluene.

Suitably the inhibitor is present in a concentration of at least 0.005% by weight of the composition, preferably about 0.01-0.03%, and optimally about 0.02%. These amounts will provide effective inhibition of free radical polymerization of the resin to increase resin loading in the composition. Furthermore, within these ranges, the desired polymerization of the resin on the workpiece will not be affected significantly by inhibitor left on the worktool caused by incomplete water washing or drying of the composition from the worktool.

EXAMPLE

In use in a test fiberglass fabrication operation, the compositions of the invention exhibit 40-60% increased loading of fiberglass resin without increased gellation as compared to the same composition without the inhibitor component therein. A typical composition performs as follows:
### Base Formula

<table>
<thead>
<tr>
<th></th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-Pyrol*</td>
<td>49.2</td>
</tr>
<tr>
<td>BLO</td>
<td>49.2</td>
</tr>
<tr>
<td>Arylene* T</td>
<td>0.1</td>
</tr>
<tr>
<td>Emulphogene* DA 630</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### Concentration (g resin/50 g. solvent) | Gellation of Base Formulation | Gellation of Base Formulation with 0.02% BHT added |
--- | --- | --- |
5 | F⁴ | F⁴ |
10 | F⁴ | F⁴ |
15 | F⁴ | F⁴ |
20 | F³ | F⁴ |
25 | F² | F⁴ |
30 | F¹ | F⁴ |
35 | G (∼ 80%) | F⁴ |
40 | G (> 90%) | F⁴ |

F = Fluid (no gel)
G = Gelled in 24 hrs. (Parenthesis indicates % gellation)

1. Gelled ∼80% in 72 hrs.
2. Gelled ∼70% in 144 hrs.
3. Gelled 5% in 144 hrs.
4. Still fluid after 30 days.
CLAIMS:

1. A resin cleaner and inhibitor composition for cleaning cured, partially cured and uncured unsaturated polyester or vinyl ester resin while reducing the rate of undesired in situ polymerization of such uncured, unsaturated polyester or vinyl ester resin in the presence of an organic solvent containing a free radical polymerization initiator comprising N-methyl-2-pyrrolidone solvent and at least about 0.005% by weight of the composition of a substituted phenol free radical polymerization inhibitor therein to suppress the rate of such undesired free radical polymerization.

2. A composition according to claim 1 wherein said substituted phenol polymerization inhibitor is selected from vanillin, 4-butylcatechol, hydroquinone and butylated hydroxy toluene.

3. A composition according to claim 1 or 2, further comprising at least one member selected from the group consisting of a diluent, an odor masking agent and a surfactant.

4. A composition according to claim 3 wherein said diluent is selected from γ-butyrolactone, a dibasic acid ester, tetrahydrofurfuryl alcohol, propylene glycol ethers, propylene carbonate, dimethyl imidazolidinone, tetramethyl urea, terpenes, and mixtures thereof.

5. A composition according to claim 4 wherein the dibasic acid ester is selected from the group consisting of dimethyl adipate, dimethyl glutarate and dimethyl succinate.

6. A composition according to claim 4 or 5 which comprises about 30-70% by weight of the composition of N-
methyl-2-pyrroldione and about 30-70% by weight of the composition of \(\gamma\)-butyrolactone.

7. A composition according to any one of claims 1 to 6 wherein said inhibitor is present in an amount of about 0.01 to 0.03% by weight of said composition.

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PATENT AGENTS