

## Applications of Vernonia Oil in Coatings

D.L. Trumbo, J.C. Rudelich, and B.E. Mote

One of the more serious issues facing today's global community is preservation of the environment. A major part of this preservation effort is limiting the amount of contaminants introduced into the air and water of the planet. The paint industry shares these concerns and over the past two decades has made much progress in bringing more environmentally friendly products to the marketplace (Chatta 1980; Padget 1993; Nabauurs et al. 1996; Bhabé and Athawale 1997). Of prime concern has been the removal or reduction of volatile organic compounds (VOC) in paint and coatings formulations, as these substances can contribute to air pollution.

Approaches to limiting VOC content have included the introduction of very high solids (>75%) liquid coatings, powder or "solventless" coatings, and waterborne (latex) paints and coatings. In this report we will concentrate on very high solids types of coatings. Very high solids coatings can be achieved by using low molecular weight polymers which are soluble in high concentration in the chosen solvent. The resulting solution must have a viscosity in the appropriate range for the desired end use of the coating. Another approach to very high solids coating formulations is the use of reactive materials as solvents. Such materials become part of the polymeric film left behind when the coating dries or cures and does not contribute to VOC. Utilization of this approach yields formulations that are nearly solvent free.

In order to be used as a reactive solvent a molecule must have at least one and preferably two or more functional groups which are capable of reacting with moieties present in the main polymeric binder of the coating. The molecule must also be a reasonable solvent for the polymeric binder, producing solutions with appropriate viscosities. These are not the only criteria that must be met, particularly in regards to specific end uses, but they are the most important.

An examination of the structure of vernonia oil, Fig. 1, obtained from *Vernonia galamensis* (Cass.) Less., Asteraceae, shows that there are three epoxy groups/molecule of oil. Epoxy groups, even hindered ones such as those in vernonia oil, possess a relatively high degree of reactivity when compared with many other moieties. Additionally vernonia oil itself has a viscosity at ambient temperature which is in the useful range. Vernonia oil then meets two of the requirements of a material being considered for use as a reactive solvent. What was not known at the beginning of this work was vernonia oil's solvent power for various types of synthetic polymers. Thus, the first part of our investigation involved synthesizing styrene containing copolymers using vernonia oil as the solvent for the polymerization. The second part of our investigation involved the use of vernonia oil as a crosslinking agent for thermally curable coatings. We believe this two phase investigation will yield information as to the suitability of using vernonia oil in reactive solvent applications.

### EXPERIMENTAL

Refined vernonia oil was obtained from Vertech Inc. of Plano, Texas and was used as received. All other chemicals were commercial grade materials and were used without further purification. Molecular weight measurements were made with a GPC equipped with a Waters 510 pump, 410 refractive index detector and two 30 mm Polymer Labs Linear microstyrigel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve solvent resistance was assessed as the number of

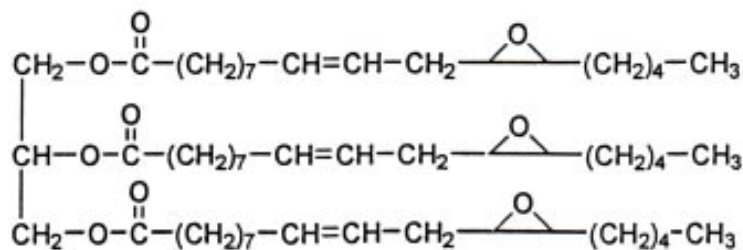


Fig. 1. Structure of vernonia oil.

methyl ethyl ketone double rubs required to break through a paint or coating film to the substrate below. The number of double rubs was measured by using an ATLAS AATCC crockmeter. Gloss measurements were made with a BYK-Gardner Microtrigloss meter. Impact measurements were made with a Gardner Impact tester employing a 4 lb weight. Pencil hardness was estimated with ASTM standard pencils.

### **Polymer Synthesis, Vernonia Oil Solvent**

Vernonia oil (370 g) was charged to a 1 liter round bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, and pressure equalizing addition funnel. The vernonia oil (after sparging with N<sub>2</sub>) was heated to 80°C with stirring and a mixture consisting of styrene (40 g), glycidyl methacrylate (24 g), n-butyl acrylate (136 g) and Vazo 64 (2.0 g) was added drop wise from the addition funnel over the course of 2 hr. After the addition was complete, another 0.3 g of Vazo 64 was added and the reaction mixture was stirred at 80°C for another 1.5 h to ensure complete conversion of monomer to polymer. Solution viscosity = 330 centipoise, Mn = 8000, mol. wt. = 17000.

### **Maleinized Linseed Oil**

This material was synthesized from linseed oil and maleic anhydride via the procedure of Warth et al. (1997). The chemical analysis and physical properties matched these given by Warth for this material.

### **Coatings Formulation (UV Cures)**

Coatings were formulated by mixing 25 g of the vernonia oil acrylic copolymer solution with the desired type and level of cure catalyst. Films were made by drawing the coating formulations over glass or aluminum panels with a #3 Bird bar (dry film thickness ~ 2 mils). The films were cured by passing the panels through a Fusion P-300 UV Cure instrument operating at a wavelength of 285–350 nm with a energy output of 1040 J/cm<sup>2</sup>. The exposure time for each panel was 80 seconds.

### **Coatings Formulations (Thermal Cure)**

Coatings were formulated by mixing stoichiometric (based on active functional groups) amounts of polymeric resin with vernonia oil. Because some of the polymeric resins employed had limited solubility in vernonia oil, it was necessary to add 25 wt % of an organic solvent (methyl ethyl ketone) to insure a homogeneous coating formula. Films were made by drawing the coating formulations over aluminum panels, as described above. The films were cured by baking in a forced air oven at 130°C for varying lengths of time. The panels were removed from the oven and allowed to cool ambient temperature before testing was begun.

## **RESULTS AND DISCUSSION**

A summary of the results obtained from the UV cure study are presented in Table 1. Controls for these experiments were films made with vernonia oil alone, the styrene-acrylic alone and the vernonia oil/styrene acrylic copolymer solution without any added cure catalyst. Both the vernonia oil alone and the styrene-acrylic alone had cure catalysts added; 6974 for the vernonia oil and 6990 for the styrene-acrylic polymers.

The vernonia oil alone, with 6 wt % catalyst added, achieved 8–12 MEK double rubs before breakthrough to the substrate. However, the films were somewhat tacky and very soft. The styrene-acrylic resin itself gave films with 30–35 MEK double rub resistance before breakthrough to the substrate. The vernonia oil acrylic achieved 2–4 MEK double rubs.

The gloss readings for the films are very low. This is because the cured films had a significant amount of surface wrinkling. However, this part of our study did show that cured films with reasonable solvent resistance and hardness could be obtained. In addition, we showed that vernonia oil is a reasonable solvent for certain types of styrene-acrylic polymers.

Because most coating applications require films without surface wrinkling, and to test the reactivity of vernonia oil as a crosslinking agent, we decided to investigate the incorporation of vernonia oil into thermoset types of coatings. This part of the study will help guide the choice(s) of polymer resin(s) to be used with vernonia oil in the formulation of very high solids systems. Additionally, the heat applied to thermoset systems allows the polymers in the film to be more mobile for a longer period of time before the onset of cure.

**Table 1.** UV cure results.

Sample	Substrate	Cure catalyst	Cure catalyst <sup>z</sup> level (wt%)	Methyl ethyl <sup>y</sup> ketone double rubs	Pencil <sup>x</sup> hardness	60° <sup>w</sup> gloss
1	Al	6990	2.0	4	--	14
2	Al	6990	3.0	5	--	7
3	Al	6990	4.0	7	--	6
4	Al	6990	6.0	6	H	6
5	Glass	6990	2.0	7	--	--
6	Glass	6990	3.0	11	B	--
7	Glass	6990	4.0	22	B	--
8	Glass	6990	6.0	35	B	--
9	Al	6974	2.0	6	--	16
10	Al	6974	3.0	8	F	21
11	Al	6974	4.0	12	F	25
12	Al	6974	6.0	16	HB	28
13	Glass	6974	2.0	25	2H	--
14	Glass	6974	3.0	28	2H	--
15	Glass	6974	4.0	33	4H	--
16	Glass	6974	6.0	40	4H	--

<sup>z</sup>Curing agents were Cyacure 6974 and Cyacure 6990 from Union Carbide.

<sup>y</sup>The number of methyl ethyl ketone double rubs required to break through a film is a measure of cure. The greater the number of rubs the higher the degree of cure is judged to be.

<sup>x</sup>Pencil hardness is ranked from softest to hardest as follows: 3B, 2B, B, HB, F and H-8H.

<sup>w</sup>Gloss measurements are measurements of reflected light and are therefore not made on films drawn on glass.

**Table 2.** Polymer binder resin data.

Polymer	Composition <sup>z</sup>	Mn	mol. wt.	Tg (°C) <sup>y</sup>
Acid functional styrene-acrylic	Styrene/butylacrylate/acrylic acid	6000	8100	70
Amine functional styrene acrylic	Styrene/laurel methacrylate/amine monomer	6400	10300	50
Maleinized linseed oil	Linseed oil/maleic anhydride	1100	1200	--

<sup>z</sup>Exact monomer percentages of the acrylic copolymers is proprietary information.

<sup>y</sup>Tg = glass transition temperatures, the temperature at which a molten or fluid material becomes an amorphous solid.

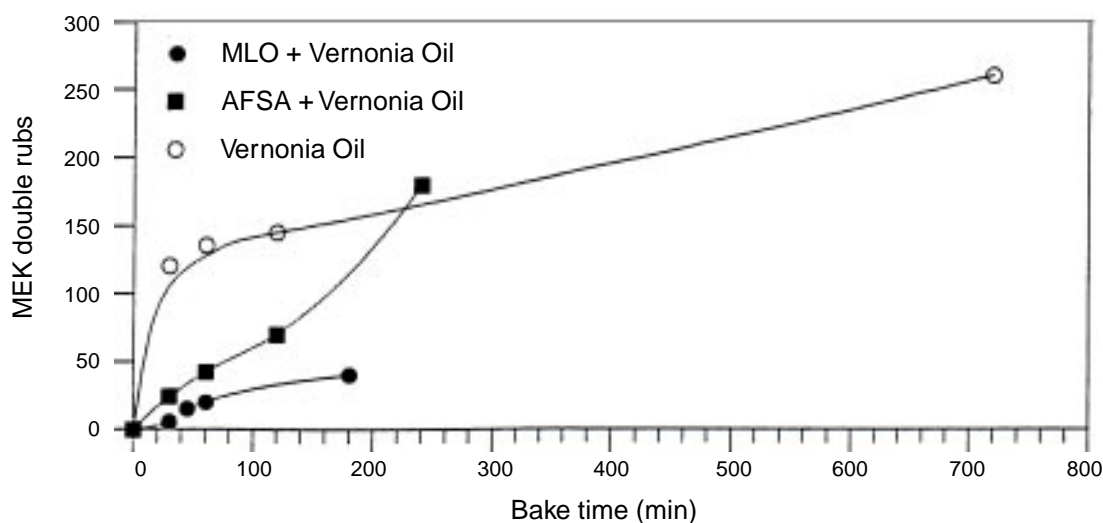
Accordingly, we blended vernonia oil with an acid functional styrene-acrylic copolymer, an amine functional styrene acrylic copolymer, and maleinized linseed oil. As previously stated a solvent, methyl ethyl ketone, was added at the 25 wt % level to obtain homogeneous formulations. Table 2 summarizes the acrylic copolymer and maleinized linseed oil data.

The film properties obtained from these resins cured with vernonia oil are summarized in Table 3. In these experiments two controls were used: vernonia oil alone and each resin alone. The vernonia does not cure under these conditions, even after heating at 130°C for 20 h. Only one or two methyl ethyl ketone double rubs were required to break through to bare metal. The maleinized linseed oil by itself attained 5–6 double rubs after 10 h at 130°C. The AFSA resin has 15–20 double rubs after 10 h at 130°C. The AMSA resins achieves 24 double rubs after 6 h at 130°C.

**Table 3.** Thermal cure results.

Starting resins <sup>z</sup>	Bake temp (°C)	Bake time (h)	Methyl ethyl ketone double rubs	Pencil hardness	60° gloss
MLO	130	0.50	6	3B	80
MLO	130	0.75	15	B	72
MLO	130	1.00	20	HB	78
MLO	130	3.00	40	H	75
AFSA	130	0.50	24	B	60
AFSA	130	1.00	42	F	72
AFSA	130	2.00	70	2H	81
AFSA	130	4.00	180	6H	88
AMSA	130	0.50	120	HB	96
AMSA	130	1.00	135	H	95
AMSA	30	2.00	145	2H	94
AMSA	130	12.00	260	4H	92

<sup>z</sup>MLO = Malenized linseed oil; AFSA = acid functional styrene-acrylic; AMSA = amine functional styene-acrylic

**Fig. 2.** Methyl ethyl ketone double rubs vs. bake time.

These results demonstrate that the vernonia oil is capable of crosslinking acid, anhydride, and amine functional resins. Not surprisingly, the reaction with the amine functional resins is the most rapid giving a relatively large number of methyl ethyl ketone double rubs in a shorter bake time. The AFSA resin also yields films with high degrees of cure if the films are allowed to bake long enough. The MLO resin attains the lowest double rub resistance, but this is not unexpected given that the degree of functionality. The MLO is less than the other two resins. However, as the plot in Fig. 2 shows, the cure response of the MLO is the same as that of the other resins; i.e. the degree of cure is increasing with increasing bake time.

The gloss numbers do show much higher values for the thermally cured films than for the UV films. This is despite the greater degree of crosslinking in the thermal films. The increased temperature does indeed allow for more polymer flow hence more uniform films with higher glosses.

## CONCLUSIONS

The results of this study have shown that vernonia oil is a reasonable solvent for styrene acrylic copolymers (Dirlikov et al. 1990; Dirlikov and Friechinger 1991). These copolymer plus vernonia oil systems can be cured cationically using photoinitiators. However, the films are wrinkled and low in gloss (Crivello and Carlson 1996). In order to further assess the reactivity of vernonia oil and to produce films with higher gloss, vernonia oil was used as a crosslinker for several polymers containing moieties known to react with epoxy groups. In all cases, the vernonia did indeed act as a crosslinker, producing films with high methyl ethyl ketone double rub resistance if baked for a sufficient time. The films cured thermally also had higher glosses. This study showed that vernonia oil has three important attributes of a reactive solvent, reasonable solvating power, good reactivity and suitable viscosity. Work is in progress concerning optimization of vernonia oil based coatings with regard to specific applications requirements.

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