

Terpene–Anhydride Resins as Coating Materials

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SYNOPSIS

Low to moderate molecular weight terpene–anhydride resins were synthesized and evaluated in coatings applications. The terpenes used were terpinolene, β -pinene, and alloocimene. The comonomers used were maleic or itaconic anhydride. The terpene–anhydride resins were used to formulate solvent-borne coatings with an epoxy or diol as a coreactant. The coatings were evaluated as films over aluminum or steel panels. When a diol was used as a coreactant, the film properties were relatively poor. When epoxy was used as a coreactant, the properties of the films were much improved in terms of resistance to solvent and hardness. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

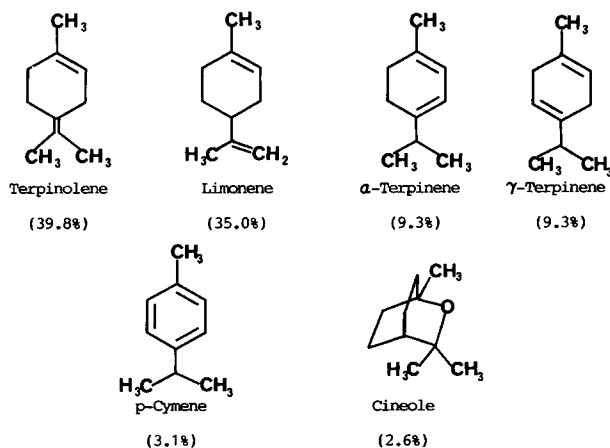
Terpene-based resins have been used for many years in commercial applications such as adhesives, printing inks, coatings, and tackifiers.^{1–4} The most commonly used resins are those based on α - and/or β -pinene, limonene, and alloocimene. However, it has been known for some time that other terpenes, for example, terpinolene and α - and γ -terpinenes, will react with unsaturated anhydrides to form polymers/oligomers.^{5,6} But the nature of these materials is not well known and no work has been done concerning the evaluation of these resins in coating applications. Therefore, we decided to investigate the synthesis of oligomers/polymers from one of these terpenes, terpinolene, and maleic or itaconic anhydride and evaluate the properties of films made from such materials. Unfortunately, at the time this investigation was started the purest grade of terpinolene we could obtain commercially contained only ~ 40 wt % terpinolene. Attempts to obtain a purer grade of material were unsuccessful, so we investigated the copolymerization of the commercial mixture with maleic or itaconic anhydride and evaluated the products obtained in coating applications. For comparison purposes polymers were synthesized from β -pinene or alloocimene and maleic or itaconic anhydride and films obtained from these materials

were evaluated in the same manner as films made with terpinolene-based materials.

EXPERIMENTAL

General

All solvents used were reagent grade and were used without further purification. The alloocimene, maleic anhydride (MAH), itaconic anhydride, terpineol, neopentyl glycol, aluminum acetylacetonate, and benzoyl peroxide (BPO) were obtained from Aldrich and were used as received. The epoxy used was Araldite CT6060 from Ciba-Giegy that had an epoxy equivalent weight (EEW) of 187. The terpinolene was obtained from SCM Glidco Organics and was part of a mixture of materials, the structures and weight percents of which were as follows:



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β -Pinene was also obtained from SCM Glidco Organics and was used as received. Infrared spectroscopy was performed on a Nicolet 5D \times B FTIR spectrometer. The spectra were obtained on either KBr pellets or neat films (NaCl plates) of the resins. The NMR spectra were obtained with a Perkin-Elmer R32 90-MHz CW spectrometer or a Varian Gemini 300-MHz FT NMR spectrometer. All the spectra were obtained on 10–15% w/v solutions in CDCl_3 or d_6 -DMSO at ambient temperature using tetramethyl/silane (TMS) as an internal standard. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with 10^6 , 10^5 , 10^4 , 10^3 , 500, and 100 Å microstyrigel columns. Tetrahydrofuran (THF) was used as the eluent and numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Terpinolene–MAH Resin (Resin 1)

A 250-mL, round-bottom flask equipped with a mechanical stirrer, reflux condenser, and thermometer was charged with 110.0 g of commercial terpinolene mixture (CTM) followed by 81.4 g of finely ground MAH. Upon addition of the MAH to the CTM, the liquid immediately turned bright yellow in color. Heating of the reaction mixture to 185°C was started. At $\sim 80^\circ\text{C}$ the reaction mixture became a homogeneous liquid. At 160°C an exotherm occurred that raised the temperature of the reaction mixture to 175°C. The heating mantle was lowered but the temperature of the reaction remained at 170–175°C for 15 min. After the temperature began to decrease, external heating was resumed and the reaction mixture was maintained at 185°C for 1 h. The total heating time, including the time taken to bring the reaction mixture to 160°, and the exotherm, was 3 h. After 1 h at 185°C, the color of the reaction mixture was dark orange and the viscosity very low. However, on cooling to ambient temperature, the viscosity increased to the point where the material was difficult to pour. The resin was heated under a vacuum of 3.0 mm to remove any volatile material. About 17–20 g of distillate was collected and proved to be a mixture of MAH, α - and γ -terpinene, cymene, and cineole, with MAH being the major component.

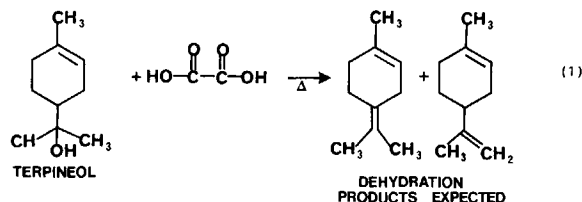
Terpinolene–MAH Resin BPO Catalyst (Resin 2)

In an attempt to increase the average chain length of the terpinolene based resins, BPO was added to the reaction mixture. The CTM (78.33 g) was charged to a 250-mL flask equipped as described

above. AH (52.7 g) followed by 1.87 g of 70% BPO was then added to the flask. Heating of the flask contents to 185°C was begun. When the temperature reached ~ 85 – 90°C , an exotherm commenced that quickly increased the temperature of the reaction mixture to 110°C. The heating mantle was immediately lowered and the exotherm was allowed to subside (~ 20 min). External heating was resumed and the reaction mixture was maintained at 185°C for 1 h. The hot reaction mixture was poured into a jar and allowed to cool overnight. As above, the cooled material was a very viscous amber resin. The resin was subjected to the vacuum distillation conditions previously described and the composition of the distillate was virtually the same as that of resin 1 in terms of types of compounds present. The relative amounts were slightly different however, with less MAH being present.

Terpinolene Synthesis by Dehydration

In an attempt to obtain a purer terpinolene, i.e., a material that contained a higher weight fraction of terpinolene, a synthesis of terpinolene by dehydration of terpineol was attempted.⁷



Dehydration of Terpineol

Terpineol (182 g) was charged into a 2-L flask equipped with a mechanical stirrer and adapted for distillation. Oxalic acid (500 g) followed by 300 mL of water was added to the flask. The reaction mixture was heated to 100°C and a mixture of water and oil began to distill. The reaction was allowed to proceed for 8 h. The water and oil layers were separated and the oil layer was dried with Na_2SO_4 . The oil layer was distilled from CaH_2 at atmospheric pressure. The distillate was collected as a single fraction boiling at 173–176°C. The distillate was water-white in color (yield 44.7%). The product composition of the distillate as measured by GC was: terpinolene, 20.3%; limonene, 10.6%; *p*-cymene, 17.6%; α - and γ -terpinene, 44.7%; unknown, 6.8%. Obviously, under these conditions, a considerable amount of bond rearrangement took place and the yield of terpinolene was considerably less than was hoped. In fact terpinolene made up less of the mixture in the present case than it did in the CTM. However, the ma-

Table I Resin Synthesis Conditions and Characterization

Resin	Terpene	Anhydride	Crude ^a Yield (wt %)	Purified Yield (wt %)	N_n	N_w	M_w/M_n
1	CTM	MAH	87.0	—	470	580	1.23
2	CTM	MAH	89.0	—	560	830	1.48
3	DTM ^b	MAH	48.0	—	340	500	1.47
4	CTM	Itaconic	50.0	—	630	780	1.24
5	β -Pinene	MAH	80.0	50.0	8100	25900	3.20
6	β -Pinene	Itaconic	61.0	45.0	4400	7000	1.59
7	Alloocimene	MAH	85.0	60.0	1200	2000	1.67
8	Alloocimene ^c	MAH	—	—	1000	2500	2.50

^a Crude yield = weight of nonvolatile material obtained.

^b DTM, terpinolene monomer mixture obtained from the dehydration of terpinol.

^c A commercial alloocimene polymer-MAH adduct obtained from Union Camp.

terial obtained from dehydration was used in the synthesis of a resin.

Terpinolene (Dehydration)-MAH (Resin 3)

The terpinolene mixture (40 g) obtained from the dehydration of terpineol was charged into a 100-mL, round-bottom flask equipped as previously described. MAH (36 g) was added and heating to 185°C was started. At 165°C an exotherm occurred that raised the temperature of the reaction mixture 10°C. The exotherm lasted for ~ 5 min and then the temperature began to decrease, at which point external heating was resumed. The reaction mixture was kept at 185°C for 1 h. The reaction mixture was worked up as described above. A large quantity of volatile material (50–60% of total product weight) was obtained, the majority of which was *p*-cymene and α - and γ -terpinenes.

Terpinolene-Itaconic Anhydride Resin (Resin 4)

The CTM (98.7 g) was charged into a 250-mL flask equipped as previously described. Itaconic anhydride (60.4 g) was added and heating to 185°C was started. When the temperature of the reaction mixture reached 170°C a very mild exotherm (2.4°C) occurred. The reaction mixture was maintained at 180°C for 1.5 h. On cooling to ambient temperature the reaction mixture gained very little in viscosity, in contrast to the behavior of the terpinolene-MAH resins. The reaction mixture was subjected to vacuum distillation and ~ 50 wt % of the reaction mixture was removed as volatile products. The composition of the distillate was itaconic anhydride, terpinolene, limonene, α - and γ -terpinene, and *p*-cymene. The residue was quite viscous, comparable to the MAH-terpinolene resins.

β -Pinene-MAH (Resin 5)

A 250-mL, round-bottom flask equipped with a magnetic stirrer, reflux condenser, and a thermometer was charged with β -pinene (35.0 g), MAH (25.2 g), and di-*t*-butyl peroxide, DTBP (0.81 g). Heating to 130°C was started. At 120°C an exotherm commenced that quickly raised the temperature of the reaction mixture to 210°C before a cooling bath could be applied. After 3–5 min in a cooling bath (H₂O, 10°C), the temperature of the reaction mixture began to decrease. When the temperature of the reaction mixture reached 20–23°C, the cooling bath was removed. The reaction mixture was a solid mass at this time, that proved insoluble in CHCl₃, CH₂Cl₂, toluene, or xylene, but was very soluble in dimethyl formamide (DMF). The product was purified by precipitation from DMF solution into a 9:1 v/v mixture of 1,2-dichloroethane/diethylether. The precipitated polymer was dried *in vacuo* at 25°C for 5 days.

β -Pinene-Itaconic Anhydride (Resin 6)

β -Pinene (33.9 g) was charged into a 250-mL flask equipped as described above. Itaconic anhydride (27.9 g) and DTBP (0.92 g) were charged to the flask and heating of the reaction mixture to 100°C was started. When the temperature reached 90°C an exotherm occurred that increased the temperature of the reaction mixture to 120°C. The temperature of the reaction mixture remained at 120°C for 5 min, then began to decrease. At this point external heating was resumed and the reaction mixture was maintained at 120°C for 2 h. When the reaction mixture cooled to ambient temperature, two layers were evident. The bottom layer was a solid orange mass, and the top layer a light yellow liquid. The liquid layer was decanted and the solid layer was

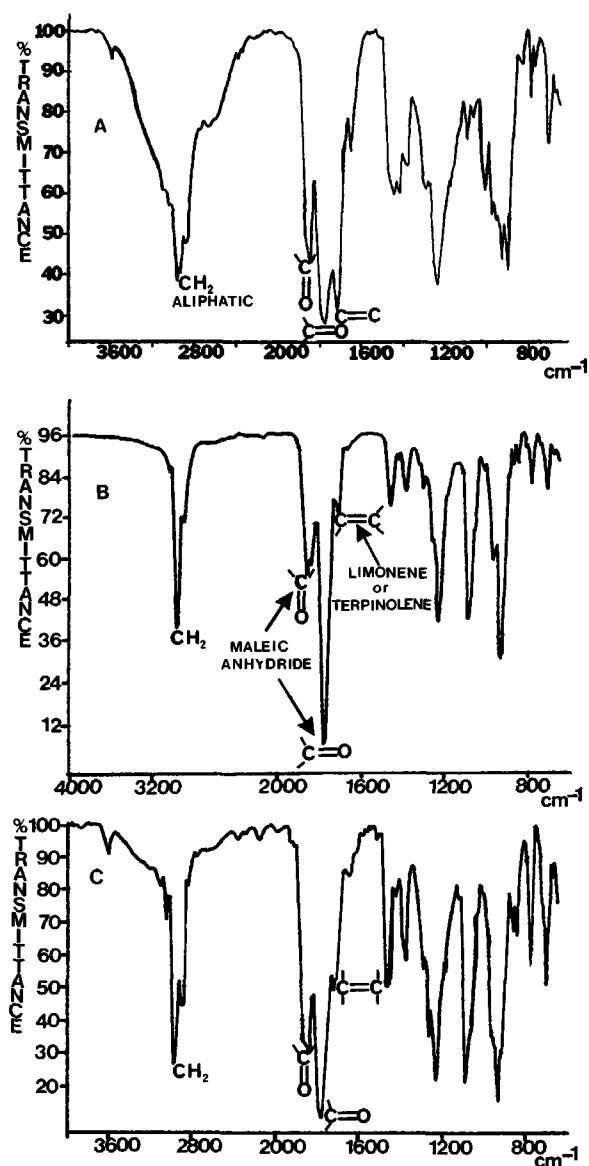


Figure 1 FTIR spectra of (A) resin 4; (B) resin 1; (C) resin 3.

purified by dissolving it in dimethyl sulfoxide (DMSO) and precipitating the polymer by addition to excess CHCl_3 /diethyl ether (50/50, v/v). The polymer was isolated by filtration and dried *in vacuo* at 25°C for 5 days.

Alloocimene-MAH (Resin 7)

Alloocimene (45.1 g) was charged into a 250-mL flask equipped as previously described. MAH (32.5 g) and DTBP (1.15 g) were charged to the flask and heating of the reaction mixture to 100°C was started. On reaching ~85°C an exotherm occurred that rapidly increased the reaction temperature to 200°C before external cooling could be applied. When the

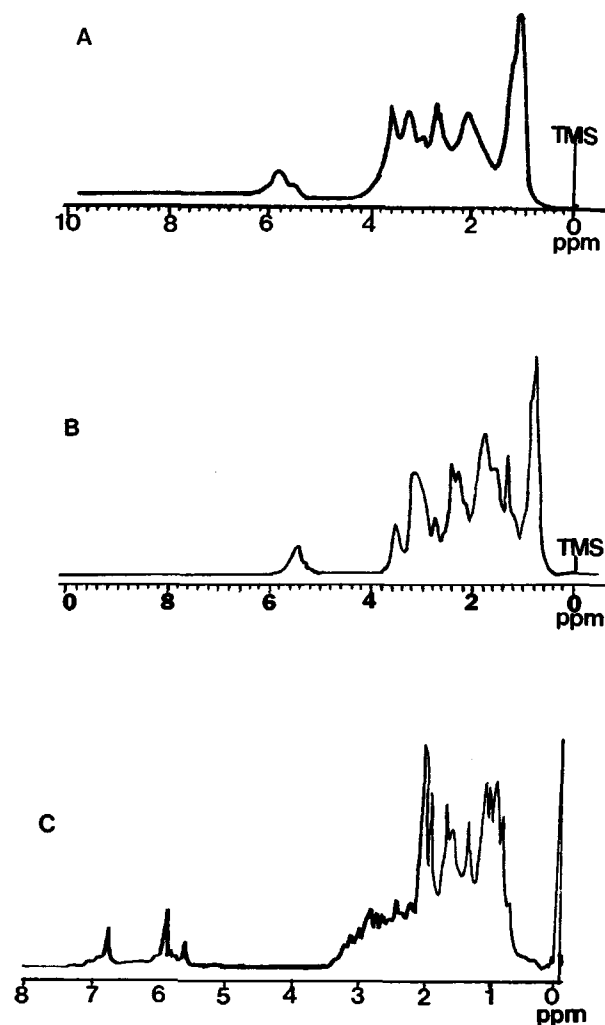
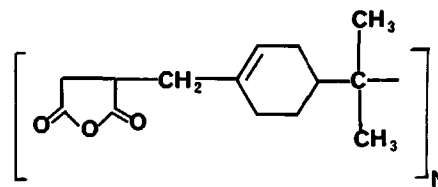


Figure 2 $^1\text{H-NMR}$ spectra: (A) 300-MHz spectrum of resin 1; (B) 300-MHz spectrum of resin 6; (C) 90-MHz spectrum of resin 4.

temperature of the reaction mixture reached 100°C, external heating was resumed. The reaction mixture was maintained at 120°C for 2 h. After cooling to ambient temperature the reaction product was a viscous amber liquid. The polymer was purified by dissolving the liquid in CHCl_3 and adding the solution to excess hexanes/diethyl ether (75/25, v/v). The precipitated polymer was isolated by filtration and dried at 25°C *in vacuo* for 5 days.



Scheme 1 Copolymer composition.

Table II Solvent Resistance

Resin	Resin Cocomponent	Bake Time (h)	Panel Type	MEK Double Rubs	
				Control	Catalyzed
1	NPG	1.0	Al	2	8
3	NPG	1.0	Al	3	9
4	NPG	1.0	Al	2	9
8	NPG	1.0	Al	2	14
1	Epoxy	1.5	Al	37	62
2	Epoxy	1.5	Al	32	46
3	Epoxy	1.5	Al	32	99
4	Epoxy	1.5	Al	100	392
5	Epoxy	1.5	Al	900	1000+
6	Epoxy	1.5	Al	575	1000+
7	Epoxy	1.5	Al	58	173
8	Epoxy	1.5	Al	33	120
1	Epoxy	3.0	Al	60	800
2	Epoxy	3.0	Al	36	900+
3	Epoxy	3.0	Al	30	900+
4	Epoxy	3.0	Al	560	900+
5	Epoxy	3.0	Al	400	400+
6	Epoxy	3.0	Al	300	400+
7	Epoxy	3.0	Al	900	900+
8	Epoxy	3.0	Al	36	350
1	Epoxy	3.0	Bond 1000	35	600+
2	Epoxy	3.0	Bond 1000	28	720
3	Epoxy	3.0	Bond 1000	35	900+
4	Epoxy	3.0	Bond 1000	80	600+
5	Epoxy	3.0	Bond 1000	410+	900+
6	Epoxy	3.0	Bond 1000	430	600+
7	Epoxy	3.0	Bond 1000	—	600
8	Epoxy	3.0	Bond 1000	32	360
Epoxy	—	3.0	Bond 1000	—	20
Epoxy	—	3.0	Al	—	30

Coating Formulation

A typical coating formulation was prepared as follows: resin 1, 20.8 g, was weighed into a wide mouth jar equipped with a magnetic stirrer followed by 16.9 g of epoxy. Solvent (methyl ethyl Ketone, MEK, 37.7 g) was added and the mixture was agitated until the resin and epoxy dissolved. The coatings were formulated on the basis of equimolar amounts of anhydride and oxirane. The amount of anhydride was estimated from the composition of the copolymers, which was determined to be ~ 50/50 (mol/mol) in all cases. The solution was divided into two parts and aluminum acetylacetonate (2.0 wt % based on solids) was added to one portion to serve as a cure catalyst. The uncatalyzed resin solution would serve as a control to evaluate the effect of the catalyst. Drawdowns of each solution were made over aluminum panels and Bondrite 1000 panels. The films were allowed to stand at ambient temperature

for 10 min so that most of the solvent could evaporate. The coated panels were then placed in a forced air oven at 150°C for the desired length of time. For the neopentyl glycol cocomponent, the coatings were formulated in the same manner except that ethyl-triphenylphosphonium bromide was used as the cure catalyst.

In all cases the drawdowns were made with a #34 wire wound drawdown bar and film thicknesses were 3.5–3.8 mil for the wet films and 1.0–1.4 mil for the dry films.

RESULTS AND DISCUSSION

The results obtained for the resin synthesis are summarized in Table I. The resins are mostly low to very low molecular weight materials (oligomers in fact), except those materials obtained from β -

Table III Impact Test Results

Resin No.	Resin Cocomponent	Bake Time	Panel Type	Impact Resistance (in./lb)			
				Control		Catalyzed	
				Forward	Reverse	Forward	Reverse
1	NPG	1.0	Al	5	5	10	10
3	NPG	1.0	Al	10	5	40	30
4	NPG	1.0	Al	10	5	20	30
1	Epoxy	1.5	Al	30	10	20	10
2	Epoxy	1.5	Al	20	20	20	10
3	Epoxy	1.5	Al	20	10	20	10
4	Epoxy	1.5	Al	70	30	20	10
5	Epoxy	1.5	Al	10	2	20	10
6	Epoxy	1.5	Al	10	4	20	10
7	Epoxy	1.5	Al	30	20	20	10
8	Epoxy	1.5	Al	10	5	20	10
1	Epoxy	3.0	Al	10	10	20	10
2	Epoxy	3.0	Al	5	3	20	10
3	Epoxy	3.0	Al	5	2	20	10
4	Epoxy	3.0	Al	30	10	20	10
5	Epoxy	3.0	Al	5	0	20	10
6	Epoxy	3.0	Al	15	0	20	10
7	Epoxy	3.0	Al	40	20	20	10
8	Epoxy	3.0	Al	20	10	20	10
1	Epoxy	3.0	Bond 1000	10	5	70	20
2	Epoxy	3.0	Bond 1000	10	10	80	20
3	Epoxy	3.0	Bond 1000	10	2	80	20
4	Epoxy	3.0	Bond 1000	40	40	80	40
5	Epoxy	3.0	Bond 1000	20	5	30	5
6	Epoxy	3.0	Bond 1000	10	5	40	5
7	Epoxy	3.0	Bond 1000	20	10	80	40
8	Epoxy	3.0	Bond 1000	40	40	80	40

pinene. The low molecular weight terpinolene materials were not purified because a suitable solvent/nonsolvent pair could not be found that would have allowed purification by reprecipitation. The β -pinene- and alloocimene-based materials could be and were purified by reprecipitation as previously described. Figures 1 and 2 show the IR and $^1\text{H-NMR}$ spectra of some of the resins synthesized for this study. The features of the spectra are assigned as shown in the figures.^{3,8,9} The IR spectra show that the resins contain MAH and aliphatic carbon absorbances. The bands at 1775–1780 and 1858–1861 cm^{-1} can be assigned to the $\text{C}=\text{O}$ group of the cyclic anhydride and bands at 925, 1080, and 1230 cm^{-1} are absorbances that are typically assigned to MAH units.^{2,3} The absorbances at 1640–1700 cm^{-1} as well as the absorbances at 2700–3100 cm^{-1} are typically assigned to the $\text{C}=\text{C}$ and $-\text{CH}_2-$ groups, respectively, of the terpene moiety. The $^1\text{H-NMR}$ spectra show broad overlapped resonances and are not particularly helpful in the evaluation of polymer

structure. However, the resonance at δ 5.71 is most probably due to a $\text{C}=\text{C}$ in the limonene units resulting from the isomerization of β -pinene (terpinolene could also isomerize yielding some limonene units). This signal was used to establish copolymer composition based on Scheme 1.^{2,3,9} The structure of terpinolene copolymers would be expected to be very similar to Scheme 1, not exactly the same, but very similar. In any case the data strongly indicate that the oligomers/polymers formed may be considered 1 : 1 (anhydride/terpene) materials.

The films were evaluated for gloss, solvent resistance, pencil hardness, and impact strength. The results obtained are summarized in Tables II–IV.

The terpene resins were tested alone, for example, with no added epoxy or neopentyl glycol (NPG), and had 2–6 MEK double rubs before breakthrough to bare metal, regardless of bake time. All the double rubs reported in Table II are the rubs required to break through the film to bare metal. The values followed by a “+” symbol shows that the test was

Table IV Pencil Hardness and Gloss Measurement Results

Resin No.	Resin Cocomponent	Bake Time (h)	Panel Type	Gloss				Pencil Hardness	
				Control		Catalyzed		Control	Catalyzed
				20°	60°	20°	60°		
1	Epoxy	1.5	Al	82.1	112.6	118.5	123.1	F	H
2	Epoxy	1.5	Al	—	—	120.9	124.3	H	2H
3	Epoxy	1.5	Al	69.8	105.0	88.8	140.8	F	H
4	Epoxy	1.5	Al	35.1	85.2	104.6	118.6	H	2H
5	Epoxy	1.5	Al	119.3	125.6	102.4	127.8	2H	3H
6	Epoxy	1.5	Al	111.0	122.9	101.0	124.5	H	2H
7	Epoxy	1.5	Al	101.1	126.5	127.5	124.0	H	H
8	Epoxy	1.5	Al	—	—	—	—	F	H
1	Epoxy	3.0	Al	91.1	119.1	114.0	124.4	2H	2H
2	Epoxy	3.0	Al	87.7	122.2	120.3	126.3	F	2H
3	Epoxy	3.0	Al	89.5	93.4	106.5	130.5	2H	2H
4	Epoxy	3.0	Al	95.6	105.9	120.6	133.2	2H	2H
5	Epoxy	3.0	Al	114.3	131.9	107.9	124.9	3H	3H
6	Epoxy	3.0	Al	127.7	126.6	128.3	130.0	2H	3H
7	Epoxy	3.0	Al	60.6	112.8	41.4	114.4	H	2H
8	Epoxy	3.0	Al	118.1	119.4	26.6	48.8	HB	H
1	Epoxy	3.0	Bond 1000	14.8	27.2	93.6	118.2	F	3H
2	Epoxy	3.0	Bond 1000	19.6	23.3	95.6	116.9	B	4H
3	Epoxy	3.0	Bond 1000	81.0	91.4	78.8	111.1	3H	5H
4	Epoxy	3.0	Bond 1000	53.0	73.9	102.6	119.8	4H	4H
5	Epoxy	3.0	Bond 1000	44.7	85.9	68.2	112.4	5H	6H
6	Epoxy	3.0	Bond 1000	96.5	100.0	71.2	104.3	5H	7H
7	Epoxy	3.0	Bond 1000	—	—	100.8	113.0	—	4H
8	Epoxy	3.0	Bond 1000	43.7	95.3	8.8	33.6	2B	H
1	NPG	1.0	Al	—	—	84.9	84.5	—	H
2	NPG	1.0	Al	—	—	94.1	104.4	—	F
3	NPG	1.0	Al	—	—	73.6	94.1	—	F

terminated at the number of rubs indicated because the solvent and the rubbing were having no effect on the film and further rubbing would have been pointless. Therefore, values of 600+, 900+, or 1000+ are effectively equal. In most cases, regardless of bake time, the presence of catalyst increased solvent resistance. In some cases the control had excellent solvent resistance after baking and the effect of catalyst was difficult or impossible to assess. The bake time also had a significant effect on the solvent resistance. Those films baked for 3 h had, in general, much improved solvent resistance in terms of MEK double rubs. This is particularly true for the catalyzed systems.

In general the β -pinene-based systems perform best, but this is expected given the greater molecular weights of the β -pinene polymers. However, the itaconic anhydride containing terpinolene resins have very good performance, even uncatalyzed and at shorter bake times. This could be due to the greater availability in terms of lack of steric hindrance, of

the anhydride moiety of itaconic anhydride compared to the anhydride moiety of MAH. However, all the terpinolene-based resins developed excellent solvent resistance when baked 3 h in the presence of 2.0% catalyst.

The films were tested for impact resistance with a Gardner Impact Tester employing a 4-lb weight. The results obtained are summarized in Table III.

In most cases the films were very brittle, with impact strengths only marginally, if at all, improved by the presence of catalyst. The films over Bondrite 1000 are an exception; the results obtained show that forward and reverse impact resistance increased significantly in the presence of catalyst in most cases. Why this should be so for the films over Bondrite 1000 and not generally for the films over aluminum is not known at the present time. In general the films from the terpinolene-based resins and those containing the alloocimene moiety had superior impact performance compared to films made from the β -pinene-based resins. Also, the films made

with the epoxy cocomponent generally outperformed those made with the NPG cocomponent.

The films were also tested for pencil hardness and for gloss. The gloss was measured with a BYK-Gardner Microtrigloss meter. The pencil hardness was measured with Berol pencils. The results obtained are listed in Table IV.

The presence of catalyst seemed to have a slight effect on gloss; the readings were, in general, slightly higher for the films in which the cure was aided by a catalyst. The pencil hardness of the films was most significantly affected by the catalyst at shorter bake times. Most probably, longer bake times gave the uncatalyzed cures the opportunity to progress sufficiently so that film properties would be nearly equal to those of films from catalyzed cures. In general the films were fairly high in gloss with the exception of the commercial alloocimene based films (resin 8). Also, the films over the aluminum panels had higher gloss than the films over the steel (Bondrite 1000) panels. However, the films over the steel panels were harder than the films over the aluminum panels. These results were not surprising, because they reflect the differences in the surfaces and material properties of the two types of panels (i.e., aluminum and steel).

CONCLUSIONS

The work described in this article shows that it is possible to produce low molecular weight oligomers of terpinolene and acid anhydrides. When these oligomers are formulated into two component coatings, films with properties comparable to more traditional terpene-based coatings can be produced provided the cocomponent is an epoxy resin. The advantages that the β -pinene- or alloocimene-based

materials have may be solely due to their greater molecular weights. In general the terpinolene-based resins had degree of polymerization (dp) of 5–8 and the resins based on β -pinene or alloocimene had dp of 25–80. The presence of cure catalyst had some effect on film properties, most significantly at shorter bake times; at longer bake times the effect was minimal.

The films produced proved to be hard, glossy, and brittle with very little impact resistance. This is not unexpected given the low molecular weight of most of these resins and the subsequently low M_c .

Work is currently underway with a purer grade of terpinolene and will be reported at later date.

REFERENCES

1. C. W. DeWalt, *Adhes. Age*, **13**, 38 (1970).
2. J. Maslinska-Solich, T. Kupka, and M. Kluczka, *Makromol. Chem. Phys.*, **195**, 1843 (1994).
3. J. Maslinska-Solich and I. Rudnicka, *Eur. Polym. J.*, **24**(5), 453 (1988).
4. E. R. Ruckel and H. G. Arle, 1983 Paper Synthetics Conference, TAPPI Proceedings, 1983.
5. P. O. Powers, *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., A. Standen, Ed., Wiley, New York, 1966, p. 11.
6. P. O. Powers, *Rubber Rev.*, **36**, 1542 (1963).
7. W. J. Roberts and A. R. Day, *J. Am. Chem. Soc.*, **72**, 1226 (1950).
8. D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, London, 1980.
9. L. M. Jackman and S. Sternhell, *Applications of NMR Spectroscopy in Organic Chemistry*, Pergamon Press, London, 1969.

Received August 26, 1994

Accepted March 24, 1995