

Color Improvement of C₉ Hydrocarbon Resin by Hydrogenation Over 2% Pd/ γ -Alumina Catalyst: Effect of Degree of Aromatic Rings Hydrogenation

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ABSTRACT: Color improvement of commercial C₉ hydrocarbon resin (c-C₉HR) and prepared C₉ hydrocarbon resin (p-C₉HR) has been investigated under various hydrogenation conditions over 2% Pd/ γ -alumina catalysts. The degrees of aromatic rings hydrogenation (DHs) and molecular structure of resin were determined from nuclear magnetic resonance of ¹H and ¹³C (¹H-NMR and ¹³C-NMR) and Fourier transform infrared spectroscopy (FTIR) analyses. The starting c-C₉HR presented in yellow color (Gardner color No. 8.4). Under the hydrogenation conditions used (H₂ pressure 70 bar, 250°C, and 8 h), the ethylenic proton in c-C₉HR was completely removed, but the aromatic rings content remained unaltered and very little change in resin color was observed (Gardner color No.8.1). On the other hand, the starting p-C₉HR contained only un-

saturated aromatic proton with Gardner color No.17.1. Under similar conditions, aromatic rings in p-C₉HR were converted to alicyclic rings, and its color was reduced to Gardner color No.5.7. By varying the DH of aromatics in p-C₉HR, two-step decolorization was observed in which at lower DH ($\leq 10\%$) the color decreased sharply from 17.1 to 9.3, while further color reduction to 5.7 was obtained when the DH was increased to 94%. It is suggested that both color body and aromatic rings were the main sources contributing to C₉HR color. Nevertheless, color stability of the resin during heat treatment was significantly improved by hydrogenation especially at DH $\geq 50\%$. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2862–2869, 2010

Key words: resins; hydrogenation; Pd/alumina; NMR; FTIR

INTRODUCTION

A C₉ hydrocarbon resin (C₉HR) is typically obtained by polymerization of reactive C₉ fraction monomers such as vinyl-toluene, alpha-methylstyrene, dicyclopentadiene, and indene using lewis acid, BF₃, AlCl₃, as initiators. The C₉HR without any post-treatment normally presents in yellow to amber color.^{1,2} The high color of resin can be used without any treatment as rubber modifier and road marking; however, many applications of C₉HR desire light color such as sealing agent, adhesive (particular the adhesive in health care products), coating agent, and varnish. In addition, the resin that contains high unsaturated parts, particularly ethylenic C=C bond, is easy to oxidize leading to high color and low heat stability. High color of hydrocarbon resin is referred to yellow to dark color including turbidity which

lead to high Gardner color No., or in other hand low Gardner color No. is represent to light color and transparent.

Hydrogenation is known as conventional method to lighten resin color. The resin with partial or completely hydrogenated unsaturated parts appears in light color.^{1,2} The hydrogenation of C₉HR can be carried out in the presence of supported metal hydrogenation catalysts under high pressure and temperature with or without solvent. The major monomers of C₉HR are indene and vinyl toluene. A simplified structure of C₉HR that has been used to explain the hydrogenation reaction in repeating unit proposed by Kim et al. are shown in Figure 1.³ The method to hydrogenate and prevent color degradation of resin during hydrogenation has been patented.^{4,5} Two stage hydrogenation was suggested for converting a high color resin to a low color resin, while softening point remains unchanged.⁶ Nickel-zinc oxide on SiO₂ and copper chromite catalysts have been used to eliminate color body of hydrocarbon resin as suggested in the US patents No. 5,817,900 and 5,491,214, respectively.^{1,2} Okazaki et al.⁷ described the C₉HR process over nickel/diatomaceous catalyst at 100–200 bar and 200–300°C. They were successful to

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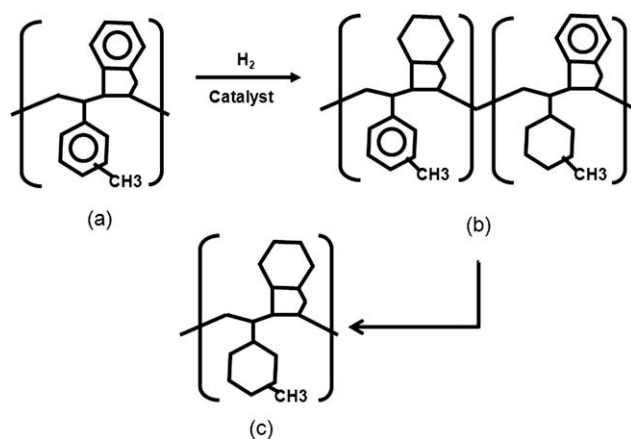


Figure 1 Scheme of C₉HR hydrogenation (a) starting C₉HR, (b) partial hydrogenation, and (c) complete hydrogenation.³

hydrogenate aromatic rings of C₉HR up to 95% as characterized by ¹H-NMR. The authors proposed that when hydrogen partial pressure and reaction temperature were lower than 30 bar and 150°C, the hydrogenation reaction was difficult to proceed. Nevertheless, the details of amount of the unsaturated proton, aromatic proton, ethylenic proton, and C₉HR color were not given.

Although hydrogenation of hydrocarbon resin is clearly one of the frequently used reactions for know how to improve color of resin, however, scientific literatures for knowledge are almost completely lacking. In this study, more detailed information about the unsaturated parts contributing to color of C₉HR and the relationship between degree of hydrogenation and color reduction of C₉HR were discussed extensively. The DHs were varied by changing hydrogen partial pressure and reaction time and were determined based on ¹H-NMR characterizations.

Materials

The c-C₉HR was obtained from Innova Chemical Co., China and used without any treatment. The p-C₉HR was polymerized using C₉ fraction monomers from SCG Chemical Co., Thailand using AlCl₃ as an initiator. The monomer fractions were approximately composed of 25 wt % indene, 18 wt % vinyl toluene, 5.6 wt % styrene, 6 wt % alpha-methylstyrene, 0.6 wt % cyclopentadiene, 0.2 wt % methyl cyclopentadiene, and balanced with other nonreactive aromatic and heavy boiling material compounds. The 2% Pd/ γ -alumina catalyst was prepared by incipient wetness impregnation method using palladium acetylacetonate (γ -alumina, 98% purity, and palladium acetylacetonate, 99% purity, were purchased from Sigma-Aldrich) dissolved in toluene as starting materials. After impregnation, the catalyst was dried at 110°C for overnight (12 h) and calcined at 600°C

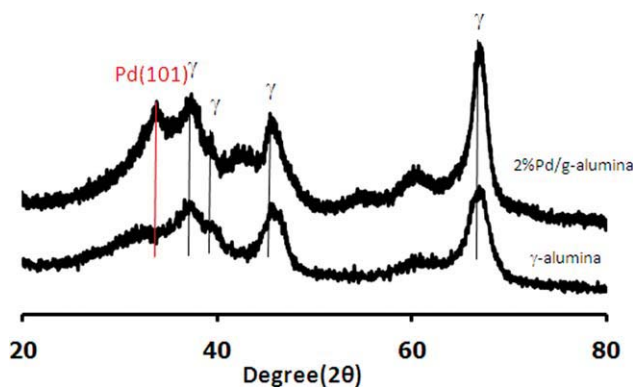


Figure 2 XRD pattern of γ -alumina support and 2% Pd/ γ -alumina catalyst. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for 10 h under air flow.⁸ Figure 2 illustrates the X-ray diffraction patterns of γ -alumina support and 2% Pd/ γ -alumina catalyst. The support shows XRD characteristic peaks of γ -phase alumina at 2 θ degrees 37°, 39°, 45°, and 66°. After loading of 2 wt % Pd, the peaks at degree 2 θ = 38° is shown and represented to tetragonal PdO(101).¹⁰ Cyclohexane (99.0% purity, A.R grade, Lab scan Asia Co.) was used as solvent without any treatment.

Reactor set up

The hydrogenation reaction was carried out using 1.2-L high pressure semi-batch reactor (Parr Instruments Co., USA Model 4520), which was equipped with magnetic driving stirrer. A schematic diagram of the reactor set up is illustrated as Figure 3. The reactor (8) was provided to operate at maximum temperature and pressure of 350°C and 345 bar, respectively. The reaction temperature was controlled by external electrically heated mantle and internal water cooling coil. The regulator (5) on the hydrogen line was connected to control hydrogen pressure fed to the reactor, pressure gauge (4) for observing hydrogen consumption during reaction. A

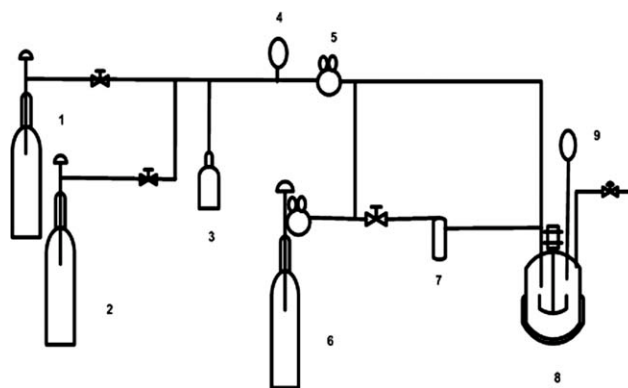


Figure 3 Scheme of the semibatch reactor set up.

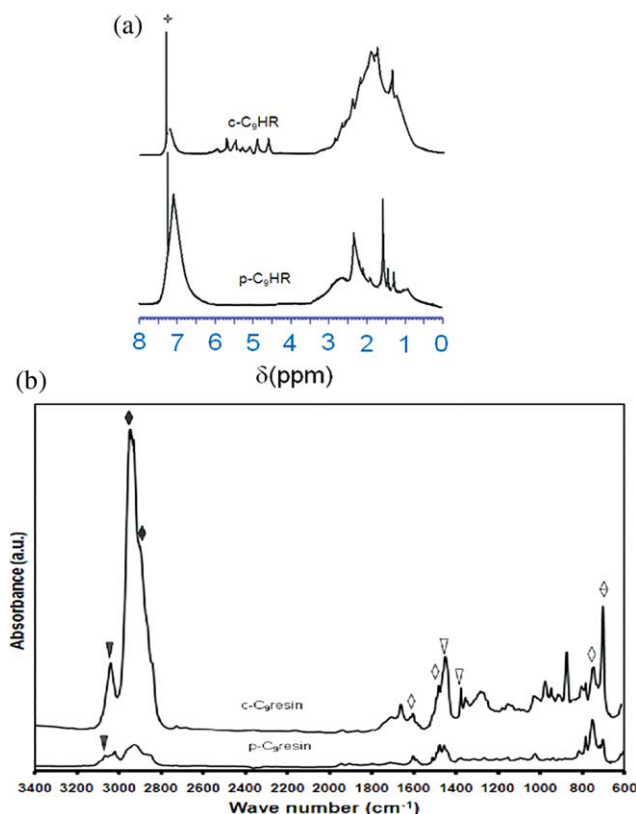


Figure 4 (a) $^1\text{H-NMR}$ and (b) FTIR spectra of p- C_9HR and c- C_9HR + is residual CHCl_3 solvent, \diamond : aromatic C—C bending, ∇ : $-\text{CH}_3$ bending, \diamond : aromatic C=C stretching, \blacklozenge : C—H aliphatic stretching, ∇ : C—H aromatic stretching. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

liquid feed vessel (7) was connected with nitrogen line for purging C_9HR solution to the reactor. No.1 and 2 were ultra-high purity hydrogen tanks and No. 3 was a hydrogen reservoir. Ultra-high purity nitrogen tank (6) was connected for air purging and liquid feeding purpose.

Hydrogenation procedure

Approximately 2 g of catalyst was first reduced *in situ* in the parr reactor with $1.5 \text{ cm}^3/\text{s}$ flow of pure hydrogen at 150°C for 1.5 h. Then, the reactor was cooled down to room temperature. After that, the reactant (110 mL of 30 wt % C_9HR in cyclohexane) was fed to the reactor using nitrogen purging gas. Hydrogen gas was initially charged to 20 psig at room temperature to protect catalytic active surface sites from inhibitor during temperature ramping. Then, the reactor was heated to 250°C . The hydrogen gas was introduced into the reactor up to desired reaction pressure and kept constant during reaction time. The reaction was started by stirring on the motor to 800 rpm. The DHs were varied by changing hydrogen pressure in the range of 10–70

bar for 0.5–8 h at 250°C . After the reaction, the solution was cooled down to room temperature in the reactor by internal water cooling coil. Excess hydrogen gas in the reactor was released with the aid of fresh nitrogen gas. The solution was kept at room temperature for 2 days for catalyst powder self-sedimentation. Then, clear solution in the upper part was completely removed by rotary evaporator.

C_9HR and hydrogenated C_9HR characterization

The C_9HR and hydrogenated resins were characterized by ^1H and ^{13}C nuclear magnetic resonance ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$, Bruker NMR 400 MHz Ultra-Shield). For a quantitative comparison, the samples were precisely prepared on 10% (w/v) in CDCl_3 solvent and operated at 25°C .^{11,12} Fourier transformed-Infrared Spectroscopy (FTIR, Nicolet 6700 FT-IR spectrometer) was operated by smart diffuse reflection mode with 0.2 g of finely grind sample to investigate the functional group. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) at the Scientific and Technology Research Equipment Centre, Chulalongkorn University, Bangkok, Thailand. Color was determined by Gardner method (Gardner color No., BYK Gardner, LCM plus instrument), and softening point was measured according to ASTM D 6493-05.

RESULTS AND DISCUSSIONS

Characterization of p- C_9HR and c- C_9HR

In this study, c- C_9HR and p- C_9HR were hydrogenated under various reaction conditions to study the effect of DH on color improvement of C_9HR . $^1\text{H-NMR}$ technique was used to identify aromatic, ethylenic, and aliphatic proton in C_9HR .^{3,7,13,14} The results are shown in Figure 4(a). The corresponding peaks in the range of 6.5–7.2 ppm were assigned to aromatic proton including aromatic proton of indene and vinyl toluene unit, whereas the peaks located at 0.4–3.4 ppm represented aliphatic proton and the peak at 2.1–2.5 ppm are proton of the methyl group ($-\text{CH}_3$) which was contacted in aromatic ring. The broad peak at around 2.3 ppm of p- C_9HR actually contained three peaks, 2.33, 2.3, 2.2 ppm which were assigned to proton of methyl in ortho, meta, and para vinyl toluene isomers,³ respectively (result not shown). Based on the $^1\text{H-NMR}$ characterizations, p- C_9HR can be distinguished from c- C_9HR . First, there was no ethylenic C=C double bond presents at 4.5–6 ppm and second, c- C_9HR was composed of more aliphatic proton than that of p- C_9HR . The amount of each proton is summarized in Table I.

TABLE I
Summary for Each Type of Proton in
c-C₉HR and p-C₉HR

Sample	%Aromatic proton ^a	%Ethylenic proton ^a	%Aliphatic proton ^a	M _w ^b	M _w /M _n ^b
c-C ₉ HR	4.3	4.3	91.4	2014	1.07
p-C ₉ HR	40.2	–	59.8	1605	1.69

^a Determined by ¹H-NMR.

^b Determined by GPC.

FTIR was used to characterize the vibration of functional groups in C₉HR and the results are illustrated in Figure 4(b). The peaks corresponding to aromatic C–C bending, –CH₃ bending, aromatic C=C stretching, C–H aliphatic stretching, and C–H aromatic stretching were apparent. The ratio of C–H aliphatic stretching peak height at 2930 cm⁻¹ to aromatic C–C bending at 700 cm⁻¹ are 2.79 and 1.4 for c-C₉HR and p-C₉HR, respectively. Such results are in good agreement with ¹H-NMR as the c-C₉HR contained much more saturated parts than p-C₉HR.

Effect of DH on color improvement of C₉HR

In this study, the DH is referred to the percent conversion of aromatic rings to cyclohexane rings as

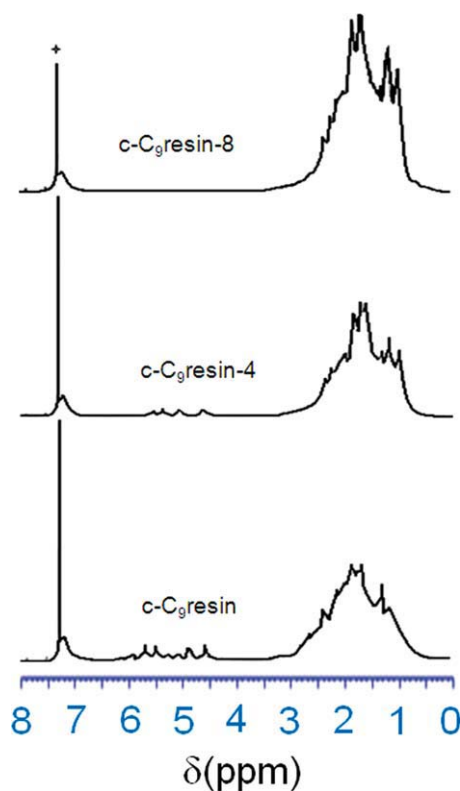


Figure 5 ¹H-NMR of starting c-C₉HR and its hydrogenated results for 4 and 8 h, respectively, over 2% Pd/γ-alumina at 70 bar, 250°C. + is residual CHCl₃ solvent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Summary of c-C₉HR and Its Hydrogenated Resin Color for Hydrogenation at 70 Bar and 250°C Over 2 g of 2% Pd/γ-Alumina and Commercial 0.5% Pd/γ-Alumina

Sample	%Aromatic proton ^a	%Ethylenic proton ^a	%Aliphatic proton ^a	Gardner color No. ^b
c-C ₉ HR	4.3	4.3	91.4	8.4
c-C ₉ HR-4	4.2	0.6	95.2	8.1
c-C ₉ HR-8	4.2	0.0	95.8	8.1
c-C ₉ HR-0.5 ^c	4.2	3.7	92.1	8.8
c-C ₉ HR-2 ^c	4.2	2.0	93.8	8.6

^a Determined by ¹H-NMR.

^b Determined by Gardner color number method (50 wt % solution in toluene).

^c Commercial 0.5% Pd/γ-alumina catalyst

measured by ¹H-NMR. The DH was calculated using the following formula described by Okazaki et al.⁷

$$DH = \left[1 - \left(\frac{\text{area of 7 ppm hydrogenated resin}}{\text{area of 7 ppm of starting resin}} \right) \right] \times 100$$

The ¹H-NMR spectra of c-C₉HR after hydrogenation over 2% Pd/γ-alumina at 70 bar and 250°C for 4 and 8 h (referred to as c-C₉HR-4 and c-C₉HR-8, respectively) are shown in Figure 5. Under the reaction condition used, both ethylenic unsaturated parts and aromatic unsaturated parts (the peaks at 4.5–6 and 6.5–7.2 ppm) decreased simultaneously. However, it is noticed that the peak area at 4.5–6 ppm was decreased more than the peak area at 6.5–7.2 ppm, indicating that the ethylenic bonds were hydrogenated in large amount than aromatic rings. After 8 h hydrogenation reaction, the ethylenic unsaturated parts in c-C₉HR were completely eliminated while aromatic proton was not decreased. The Gardner color No. of c-C₉HR was slightly decreased from 8.4 to 8.1 after hydrogenation reaction up to 8 h as shown in Table II. The commercial 0.5% Pd/γ-alumina catalyst was also used to study decolorization of c-C₉HR under various hydrogenation conditions. At low hydrogen pressure, short reaction time, and/or low amount of catalyst used, the color of c-C₉resin was darker than original c-C₉HR as indicated by Gardner color No. > 8.4. The increase of resin color might occur during heating to a desired reaction temperature during hydrogenation reaction.

For better understanding of the color reduction of C₉HR by hydrogenation, C₉HR was prepared in our laboratory using the C₉ monomers described in materials section and denoted as p-C₉HR. The p-C₉HR presents in amber color (Gardner color No.17.1). The hydrogenation was performed at 70 bar 250°C for various times to control the DHs, and the results are shown in Table III. The p-C₉HR-50, p-C₉HR-70, and p-C₉HR-94 are referred to hydro-

TABLE III
Summary of Hydrogenated p-C₉HR for Various Times at 70 Bar and 250°C Over 2% Pd/γ-alumina Catalyst

Sample	React time (h)	DH ^a	%Aromatic proton ^a	%Aliphatic proton ^a	Gardner color No. ^b
p-C ₉ HR	0	0	40.2	59.8	17.1
p-C ₉ HR-17	0.5	17	33.5	66.5	11.2
p-C ₉ HR-50	2	50	20.0	80.0	8.8
p-C ₉ HR-70	4	70	12.0	88.0	7.1
p-C ₉ HR-89	6	89	4.6	95.4	6.2
p-C ₉ HR-94	8	94	3.0	97.0	5.7

^a Determined by ¹H-NMR.

^b Determined by Gardner color number method (50 wt % solution in toluene).

generated p-C₉HR with degree of hydrogenation 50, 70, and 94, respectively. It is shown that DH was increased from 0 to 94 when reaction time was increased from 0 to 8 h. The aromatic proton was decreased from 40.2 to 3.0%. The Gardner color No. was found to decrease simultaneously from 17.1 to 5.5. On the other hand, the aliphatic proton increased as DH increased. The ¹H-NMR, ¹³C-NMR results of hydrogenated p-C₉HR are shown in Figure 6.

The ¹H-NMR spectra of p-C₉HR with various DHs [Fig. 6(a)] show that the peak area at 6.5–7.2 ppm was significantly decreased, indicating an increase of DH. The ¹³C-NMR results between 120 to 130 ppm region [Fig. 6(b)] which were assigned to aromatic carbons of indene, ortho and meta vinyl toluene unit, show significant reduction of peak areas corresponding to an increase of DH. At the DH of 94, the broad peak at 2.3 ppm which was composed of three peaks at 2.33 and 2.3 and 2.2 ppm was observed only at 2.2 ppm. It has been explained that the ortho and meta isomers of vinyl toluene including indene unit were simultaneously hydrogenated.³ Moreover, Ness et al.¹⁵ reported similar results in which polymer hydrogenation was modeled in blocky adsorption; large fraction of carbon–carbon double bond in polymer conformation was first hydrogenated. In other words, before polymer desorbed from catalyst surface, the large carbon–carbon double bond was hydrogenated.^{16,17} This study clearly shows that Pd/γ-alumina catalyst was effective for hydrogenation of resin containing aromatic rings. Other Pd catalyst systems used for aromatic ring hydrogenation in polymer have also been reported. For example, polystyrene was achieved more than DH of 90 over Pd/Ba₂SO₄ catalyst.¹⁸ Both aromatic rings and ethylenic bonds in poly(styrene) and poly(styrene)–poly(isoprene) diblock copolymers were eliminated using Pd/Ba₂SO₄ and Pd/CaCO₃ catalysts.¹⁴ In contrast, C₉HR hydrogenation was difficult to be hydrogenated over Ni/diatomaceous earth catalyst.⁷ As reported by Nakatani et al.,¹² polystyrene with high molecular weight was capable to be hydrogenated

using Pd catalyst, whereas aromatic rings in low molecular weight of polystyrene could be completely hydrogenated by Ni catalyst.

Based on the FTIR spectra of p-C₉HR with various DHs [Fig. 6(c)], the DH was increased with the decrease of aromatic C=C stretching peak at 1489, 1610 cm⁻¹, the C–C aromatic bending at 700, 750 cm⁻¹, and C–H aromatic stretching peak at 3024 cm⁻¹. The images of color reduction for p-C₉HR after hydrogenation at various DHs are shown in Figure 7. The hydrogenated p-C₉HR with DH of 94, in this sample the color presents to near water or water

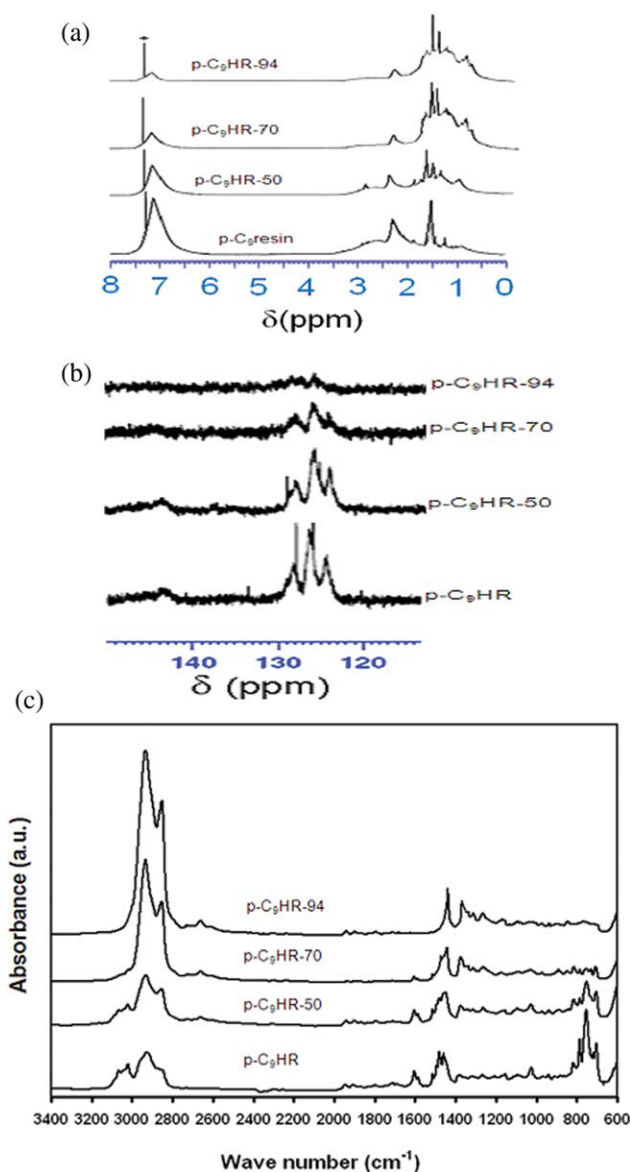


Figure 6 (a) ¹H-NMR (b) ¹³C-NMR at 115–150ppm region, and (c) FTIR spectra of p-C₉HR and its hydrogenated p-C₉HR at various DH over 2%Pd/γ-alumina at 70 bar and 250°C. + is residual CHCl₃ solvent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

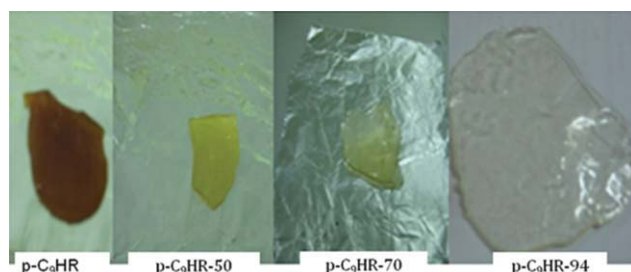


Figure 7 Color reduction of p-C₉HR at various DH over 2% Pd/γ-alumina catalyst at 70 bar and 250°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

white resin, aromatic proton was decreased to 3.0% and aliphatic proton was increased to 97.0%. According to US patent No. 5,171,793, hydrogenated resins contain 1–20% aromatic proton have near water to water white color.¹⁹ Moreover, aromatic petroleum resin with DH more than 90 is preferred for adhesive resin composition to obtain white adhesive result or colorless and transparent characteristics.²⁰

From the open literatures, the color of hydrocarbon resin may be related to color body (defined as the high conjugate compound containing polar atom),^{1,2} and fuvene structure substance.²¹ However, both of color body and fuvene substance were not detected in this work due probably to small quantity presented. Nevertheless, only small amount of these compounds can lead to yellow visible effect.²² Some documents reported that an introduction of aromatic compound into tackifier resin led to the resin with high color characteristics.¹⁹ The dark yellow to amber color of hydrocarbon resin is also believed to be due to high amount of unsaturated parts.²² Table IV summarizes the structures contributing to resin color that have been reported in the published literature. For this works, aromatic resonance bonds or phenyl rings in C₉HR were suggested to be color agents due to electron delocalization in phenyl rings. Figure 8 shows color reduction of C₉HR over DH, it was obviously observed that after Gardner color No. of 11.2 the color reduction was decreased with increasing of DH. It might be due to at high DH the

TABLE IV
Summary the Structure Contributing Resin Color

Structure	Hydrogenation condition	Reference
Conjugate C=C bound	10–150 bar, 150–300°C, Ni catalyst	1,2,13
Conjugate bound containing polar atom	10–80 bar, 150–265 °C, Copper chromite, Ni catalyst	1,2
Fuvene structure	not available	21
Aromatic rings	70 bar, 250°C, Pd catalyst	This study

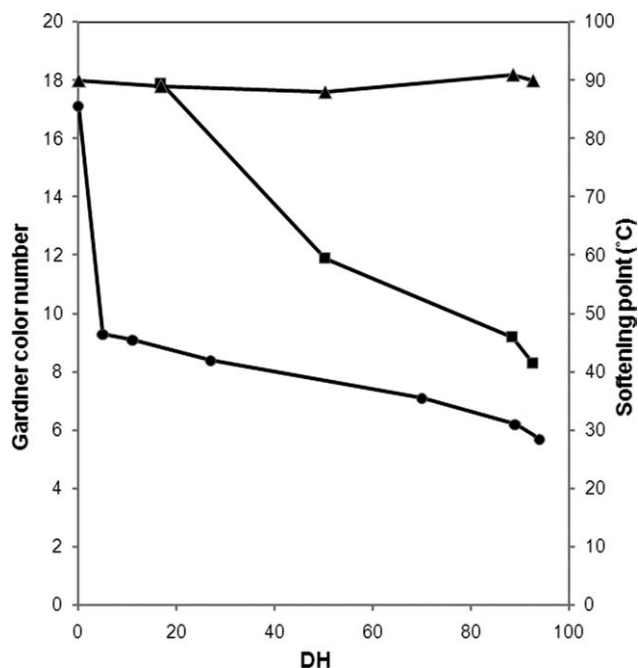


Figure 8 Plot the relation between Gardner color No. of hydrogenated p-C₉HR, color stability (after aging) of hydrogenated p-C₉HR, softening point and DH; ▲: Softening point, ■: Color after aging, ●: Color of hydrogenated resin.

amount of electron delocalization in phenyl rings of the polymers was reduced.

Further investigation on hydrogenation was carried out over p-C₉HR and Pd/γ-alumina catalyst. The results are shown in Table V. The hydrogen partial pressure of hydrogenation reaction was varied at 10, 30, 50, and 70 bar at 250°C. The use of low pressure resulted in little aromatic rings hydrogenation while high hydrogen pressure ensured aromatic ring hydrogenation.^{2,3,7,13,23,24} For example, at the reaction conditions hydrogen partial pressure 10 bar, 250°C, and 4 h, aromatic rings were converted only 5% but Gardner color No. sharply reduced from 17.1 to 9.3, suggesting that color body can probably be eliminated at low hydrogen pressure. When hydrogen partial pressure was increased to 30 bar at the same temperature, the conversion of aromatic rings was slightly increased to

TABLE V
Summary of Hydrogenated p-C₉HR for Various Hydrogen Pressures at 250°C for 4 h Over 2% Pd/γ-alumina Catalyst

Hydrogen pressure(bar)	DH ^a	Gardner color No. ^b
p-C ₉ HR	0	17.1
10	5	9.3
30	11	9.1
50	27	8.4
70	70	7.1

^a Determined by ¹H-NMR.

^b Determined by Gardner color number method (50 wt % solution in toluene).

TABLE VI
Summary of Hydrogenated Commercial Resin Over 2%Pd/ γ -Alumina Catalyst at 70 Bar and 250°C for 4 h

Sample	%Aromatic ^a	%Ethylenic ^a	DH ^a	Gardner color No. ^b	
				Before hydrogenation	After hydrogenation
A	43.4	–	17	8	6
B	33.7	2.7	20	12	8

^a Determined by ¹H-NMR.

^b Determined by Gardner color number method (50 wt % solution in toluene).

11%, but little color reduction was observed (Gardner color No. decreased from 9.3 to 9.1). Finally, the hydrogen partial pressure was further increased to 50 and 70 bar at 250°C, DH was increased to 27, 70, and Gardner color No. was reduced to 8.4 and 7.1, respectively. Color reduction at high hydrogen pressure could be due to aromatic rings hydrogenation. In addition, the optical, thermal, and oxidative properties of polystyrene were improved by converting of phenyl C–H bond in to aliphatic C–H bond.²⁵ A second example, aromatic rings in lignin, biopolymer, were hydrogenated to inhibit oxidative yellowing of paper made from mechanical pulps.^{26–29}

The other commercial C₉HRs containing different amount of proton purchased from Yuen Liang Co., Taiwan, were also used for hydrogenation. The results are summarized in Table VI. The C₉HR A contains 43.4% aromatic proton and 56.6% aliphatic proton and has Gardner color No. 8, whereas the C₉HR B composes of 33.7% aromatic proton, 2.7% ethylenic proton, 63.6% aliphatic proton with Gardner color No. 12. Both resins were hydrogenated at 70 bar and 250°C for 4 h over 2% Pd/ γ -alumina catalyst. Resin A was hydrogenated to DH of 17 and Gardner color was reduced to 6. For resin B, ethylenic proton was completely eliminated and aromatic rings were hydrogenated to DH of 20, the color was reduced to Gardner color No.8.

The color stability of hydrogenated p-C₉HR was tested according to the US patent No. 6433,104 using a ventilated oven.³⁰ The p-C₉HR with various DHs was heated from room temperature to 175° C ($\pm 5^\circ$ C) and held at that temperature for 5 h. Then, the samples were cooled down to room temperature. The Gardner color number of aged p-C₉HRs were measured in dissolved 50 wt % toluene. Figure 8 shows the relationship between DH and Gardner color No. of the initial hydrogenated p-C₉HR and the aged hydrogenated p-C₉HR. It is shown that for low DH (≤ 50), the color of resin after aging as determined from Gardner color number was increased by 37% (11.2 to 17.8), whereas for high DH (≥ 50), the color of resin was increased by 30% (5.7 to 8.3). Without hydrogenation, the color of resin after aging was very dark (Gardner color No.>18). Such results

indicate that hydrogenation of aromatic rings in C₉HR can improve both the color and color stability of resin. Although the DH was increased from 0 to 94, the softening point was not greatly changed (the line containing triangular symbol of Fig. 8), as there was no significant change in the molecular weight (M_w) and M_w/M_n of the hydrogenated resin. The molecular weight was increased about 3% due to aromatic rings hydrogenation.³

CONCLUSIONS

The aromatic rings in C₉HR were suggested to be one of the main sources contributing to resin color. Hydrogenation of aromatic rings to alicyclic rings with DH about 94% using 2% Pd/ γ -alumina catalyst reduced the color of p-C₉HR from Gardner color No.17.1 to 5.7. Color reduction at low DH, however, suggests partial eliminated of color body in the p-C₉HR, whereas at high DH, the color of p-C₉HR was reduced both color body and aromatic rings. The hydrogenated resin showed much high color stability during heat treatment compared to the nonhydrogenated resin especially at high DH. There was no change of softening point of resin under various hydrogenation conditions and catalyst used.

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