

Decoloration of Indene–Coumarone Resins by Catalytic Hydrogenation

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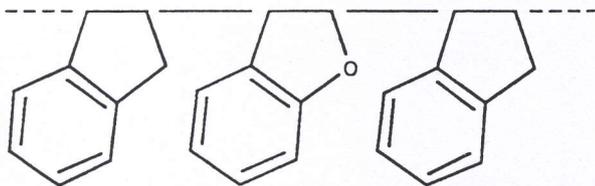
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Abstract: The catalytic hydrogenation of indene–coumarone resins, a coal-derived polymer, has been carried out using commercially available catalysts. Hydrogenation of the resins causes the saturation of double bonds and leads to decoloration of the product, increasing its market value. A nickel-on-kieselguhr catalyst (Süd-Chemie G-49-BRS) seems to be the most active and gives the highest degree of decoloration. However the decolorated resins tend to recover spontaneously their former colour, the process being only slightly prevented by the addition of stabilizers.

Key words: indene–coumarone resins, catalytic hydrogenation, polymer coloration.

1 INTRODUCTION

Indene–coumarone resins are obtained by polymerization of a coal tar fraction (b.p. between 160 and 260°C), which contains polymerizable compounds such as styrene, dicyclopentadiene, indene, coumarone, and their alkyl-derivatives. After separation of acidic and basic compounds (e.g. phenols, pyridines) and water, this fraction is polymerized, using sulphuric acid as catalyst, or more often a Lewis acid, such as boron trifluoride. The product is a copolymer with the following structure:



Tar formed during polymerization is then filtered, the catalyst is neutralized, and finally the solvent is separated from the polymerized resin by distillation.

The properties of the resin depend on the nature of the raw material, and the industrial process. Those that determine its quality are: softening temperature, viscosity, thermal stability, solubility in organic solvents, and colour.

Indene-coumarone resins were discovered by the German scientists Kraemer and Spilker in 1890.¹ They

have been widely used in industry, mainly as paint components. In the 1950s, they were displaced by aromatic thermoplastic resins derived from petroleum. Nevertheless, indene–coumarone resins are still used by several transformation industries in the production of adhesives, rubber, paint and lacquers.

1.1 Colour and stability

The price of indene–coumarone resins decreases markedly when they are dark-brown coloured, and a fraction of this type is inevitably produced in the industrial process.

There are three main causes for resin degradation and darkening: thermal oxidation, photochemical oxidation, and reaction with corrosive elements in the atmosphere. Photooxidation of organic polymers is produced by light absorption by chromophores, present in the polymer structure, or as impurities. As a result, some bonds are broken, and free radicals formed, which react in a chain process with atmospheric oxygen.²

In order to slow down the degradation process, chemical stabilizers can be added to the polymer, usually in proportion 0.1 to 1.0 wt%. Additives can work following different mechanisms:³ absorption of photons, deactivation of excited species such as $C=O^*$ and 1O_2 , decomposition of hydroperoxides, before they can absorb photons and direct reaction with free radicals.

Several mechanisms have been suggested in order to explain the coloration of indene-coumarone resins. Carmody⁴ points out that fulvenes can be formed by reaction between aldehydes or ketones. It is more likely that indene-coumarone resins react with atmospheric oxygen, producing a hydroperoxide that is transformed into degradation products as a result of a polymeric chain breaking. A similar mechanism has been proved to initiate the degradation of phenolic resins.⁵

1.2 Decoloration of indene-coumarone resins

Catalytic hydrogenation is the most suitable process for decoloration of indene-coumarone resins, as a result of the elimination of unsaturated compounds and terminal double bonds.

Studies on hydrogenation of indene-coumarone or similar resins are scarce in the literature. Carmody *et al.*⁶ studied this process at pressures up to 65 bar and above 270°C, with a Nickel-Raney catalyst, which was soon deactivated. Jones *et al.*⁷ studied the catalytic hydrogenation of a styrene-butadiene copolymer with a nickel-on-kieselguhr catalyst. Mostecky *et al.*⁸ used nickel and molybdenum sulphides to hydrogenate an indene resin at 60 bar, obtaining a product with a light yellow colour. Data on resin colour stability are not given.

Whitby and Katz⁹ studied the thermal stability of polyindene. The degradation of high molecular weight chains started at 180–190°C, while shorter chains were stable up to about 200°C. Zeltmoyer and Vanderryn¹⁰ report that the higher polymers are less stable than the low molecular weight ones.

2 EXPERIMENTAL

2.1 Materials

Industrial indene-coumarone resins were used dissolved in the aromatic process solvent, called solvent-naphtha. Resins were supplied by Industrial Quimica del Nalón

S.A. (Asturias, Spain), and were obtained by boron-trifluoride-catalysed polymerization of a coal tar fraction with a boiling point range of between 150 and 200°C. The main constituents of solvent-naphtha, determined by GC, are indene, *m*-xylene, pseudocumene and naphthalene, with smaller amounts of toluene, *o*- and *p*-xylene, styrene, cumene, coumarone, indene, durene, isodurene and benzonitrile. Commercial catalysts tested are listed in Table 1. High purity hydrogen (99.998%) and hydrogen sulphide (99.7%), and analytical grade reagents were used.

2.2 Apparatus

Two different types of apparatus were used in hydrogenation experiments: two tubing bombs and a 500 cm³ autoclave. The tubing bombs, which consisted of 35 cm³ 316 stainless steel horizontal cylinders, provided with a manometer, were introduced into a thermostated fluidized sand bath, and mechanically shaken with an up-and-down motion. The autoclave is a 316 stainless steel commercial unit Standard 500 cm³ Magnedrive II (Autoclave Burton Corblin) provided with a sampling system. When extruded or when pellet catalysts were tested, two gaskets were fixed to the internal baffles.

The experimental method was similar for both sets and consisted of the following steps: reactor feeding, pressurization, heating to reaction temperature, reaction, cooling, depressurization, and discharge. Tubing bombs were charged with 12 cm³ of liquid and ground catalyst, and then closed, purged, first with nitrogen and then with hydrogen, and pressurized with hydrogen. Afterwards, they were placed inside the preheated fluidized sand bath, and heated to the reaction temperature. After two hours of reaction, the tubing bombs were cooled with air and water, and discharged. The catalyst was separated from the reaction mixture by filtration.

The autoclave unit was charged with 170 cm³ of liquid and catalyst, purged, and pressurized with hydrogen at 5 bar. Then, heating was started, and once the desired temperature was reached and hydrogen pressure in-

TABLE 1
Characteristics of Commercial Catalysts Tested in Hydrogenation of Indene-Coumarone Resins

Symbol	Supplier	Type	Active metal	Support	Shape
A	BASF	Ni-Raney	Ni	—	Powder
B	Merck	Ni-Raney	Ni	—	Powder
C	BASF	Co-Raney	Co	—	Powder
D	Merck	Ni-Raney	Ni	—	Powder
E	Süd-Chemie	G-49-BRS	Ni(35%)/NiO(18%)	Kieselguhr	Powder
F	Süd-Chemie	T-2451-RS	Ni(51%)	Silica-alumina	0.8 mm extrusions
G	Hoechst	52/35 TS	Ni(52%)	Kieselguhr	Powder
H	Hoechst	60/35	Cu(60%)	Silica	Powder
I	Shell	S-214	NiO(2.8%)/MoO ₃ (13.5%)	Alumina	1.5 mm extrusions
J	Shell	S-324	NiO(3.4%)/MoO ₃ (19.8%)	Alumina	1.5 mm extrusions

creased to the desired value, the reaction time was taken as zero. As the reaction proceeded, 5 cm³ samples were taken at different time intervals, and hydrogen was fed to maintain the pressure.

2.3 Analytical methods

The degree of coloration of the resins was measured with a commercial optical comparator, based on the Gardner scale, which is used industrially for indene-coumarone resins. The use of this technique reassures that light absorption takes place at a low and well established wavelength. This was checked with a V-UV spectrophotometer.

The Iodine index, although primarily used for the determination of the degree of unsaturation of fats and oils, is also used for characterization of indene-coumarone resins. In this work it was found that the iodine index of indene-coumarone resins, measured by both Wijs¹¹ and Hanus¹² methods, depends on the sample weight and analysis time. This could be explained by substitution reactions between halogen halides and aromatic compounds (especially polycyclic and alkyl-substituted),¹³ this phenomenon being more important for large halide excess.¹⁴ It was also observed in this work that iodine index, measured by the Hanus method, correlates well with the inverse of the sample weight, the time of analysis remaining constant:

$$I_m = A + b/m$$

where I_m : measured iodine index
 m : sample weight
 b : constant
 A : function of the degree of unsaturation

In order to improve the reproducibility of the method, and for comparison purposes, a corrected iodine index, I_c was defined as:

$$I_c = I_m + 13.24/m$$

The resin samples (1.25 g approx.) were accurately weighed and dissolved in 10 cm³ of carbon tetrachloride, with a 2 h time of analysis. Using this correlation, no negative I_c values were obtained, and the value for hydrogenated resins was close to zero. The degree of saturation of the resins after treatment is expressed as ' % saturation', defined as $(I_{c, \text{initial}} - I_{c, \text{final}})/I_{c, \text{initial}}$. The metoxy-mercuriation method described by Das,¹⁵ was also tested for measuring resin unsaturation, giving unsatisfactory results.

Solvent-naphtha was analysed by GC (Hewlett-Packard 5710A), employing bentone and diisododecylphthalate on Chromosorb W 50-60 as stationary phase.

3 RESULTS AND DISCUSSION

3.1 Tubbing bomb experiments

Six commercial catalysts were tested in tubing bomb experiments. Indene-coumarone resins were hydrogenated either as industrially produced, in 35 wt %

TABLE 2
Results for Indene-Coumarone Resins Hydrogenation in Tubbing bomb Experiments (1-12) and Autoclave (13-18)

Experiment	Catalyst	Solvent	Cat. load (wt %)	Temp. (°C)	Initial P (bar)	Operation P (bar)	Gardner colour	Saturation (%)
1	E	Solvent-naphtha	0.5	150	35	42	12	0
2	E	Solvent-naphtha	0.5	250	25	30	11.5	9
3	E	Solvent-naphtha	5	250	35	42	10.5	54
4	E	Solvent-naphtha	7	300	45	64	5.5	66
5	E	Toluene	3	250	45	89	2.5	82
6	E	Toluene	3	300	45	93	3.5	77
7	G	Solvent-naphtha	3	250	45	93	11.5	24
8	G	Toluene	3	250	45	102	4	70
9	A	Solvent-naphtha	3	250	45	76	10	27
10	B	Solvent-naphtha	3	250	45	87	12.5	21
11	C	Solvent-naphtha	3	250	35	72	12	30
12	H	Solvent-naphtha	3	250	35	90	14.5	19
Experiment	Catalyst	Solvent	Cat. load (wt %)	Temp. (°C)	Pressure (bar)	Gardner colour	Saturation (%)	
13	I	Solvent-naphtha	3	250	80	9	22.7	
14	I	Solvent-naphtha	3	300	80	11	31.1	
15	J	Solvent-naphtha	3	250	80	9.5	55.2	
16	J	Solvent-naphtha	3	250	120	11	56.2	
17	J	Solvent-naphtha	3	300	80	11	53.2	
18	J	Solvent-naphtha	3	300	120	10.5	57.4	

solution of solvent-naphtha (initial Gardner colour 13–14), or as a solid dissolved in 50 wt % toluene (initial Gardner colour 14–15). The mass of catalyst added and reaction temperature were varied, while reaction time (4 h) was kept constant. The reaction pressure depends on both reaction temperature and hydrogen consumption, these factors being impossible to control. Experiments were planned following two-level factorial designs, with some complementary experiments.

Most representative results are summarized in Table 2. Catalyst E (Süd-Chemie G-49-BRS) was tested at 150–300°C and 25–35 bar. Decoloration was always higher when toluene was used as solvent instead of solvent-naphtha. Maximum decoloration was reached at 250°C and 3 wt % catalyst for both toluene (95% decoloration) and solvent-naphtha (74% decoloration). The general trend was higher saturation for higher decoloration.

Catalysts A, B, C, G and H, were tested at 200–250°C and 1–3 wt % catalyst (see Table 2). Results in all experiments were worse than with catalyst E. The order in decoloration activity was:

E, A, C, G, B (activated 'in situ'), H

The difference in activity between catalysts E and G, both nickel-on-kieselguhr, can be explained by stronger mass-transfer resistance in the particles of catalyst G, which are larger in size than particles of catalyst E. The low activity of Raney catalysts may be due to the presence of poisons in the feed, and to sintering processes which occur in these catalysts at temperatures above 200°C.

3.2 Autoclave experiments

Catalyst E, which gave the best results in tubbing bomb experiments, was tested in an autoclave. First, the influence of agitation speed was determined in a series of experiments, operating in conditions of 300°C, 40 bar, 1.5 wt % catalyst and agitation speeds of 1000 to 2000 rpm. Constant maximum decoloration and saturation was obtained for agitation speeds higher than 1500 rpm, and this value was fixed in subsequent experiments.

Reaction kinetics was studied by taking samples at different reaction times, up to 20 h, under different reaction conditions. Results (Fig. 1) showed that resin decoloration was very fast in the first 4 h, the process being slower for a higher reaction time, and the reaction was completed in about 10 h. Saturation was initially fast, but the saturation rate was very slow after about 4 h. Several hydrogenation experiments were duplicated, and the reproducibility of the results was very good.

Colour and per cent saturation after 4 h reaction time, temperature 200, 250 and 300°C, and pressure 40, 80 and 120 bar are shown in Fig. 2. The degree of saturation of the resin increased as the temperature and pressure

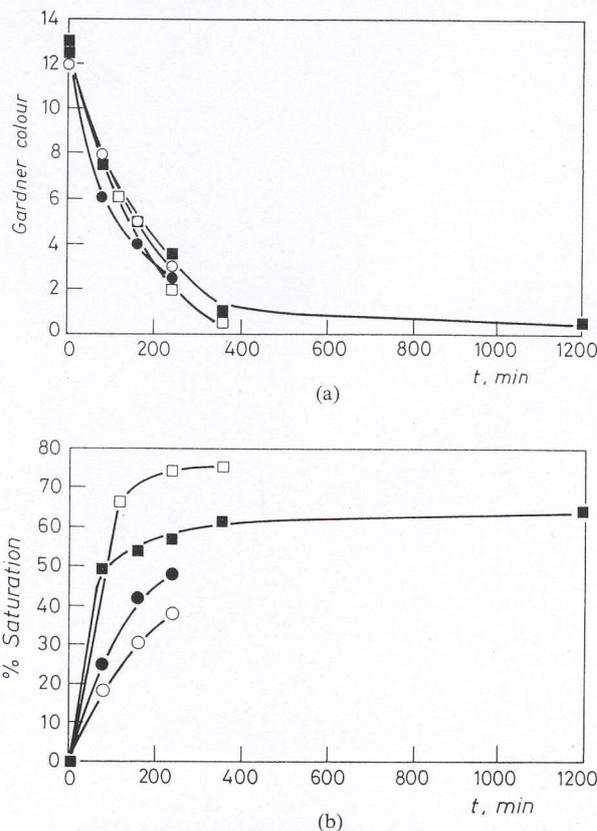
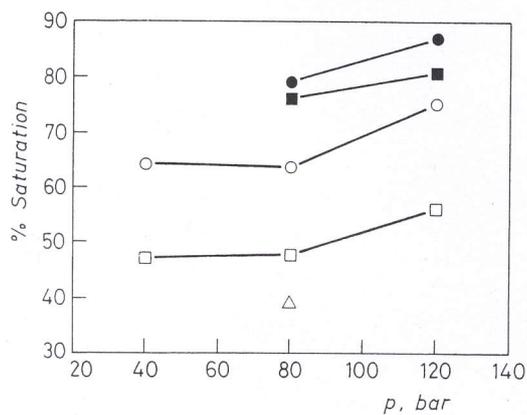


Fig. 1. Evolution of resin Gardner colour (a) and saturation (b) with reaction time for hydrogenation with 1.5 wt % catalyst E at different reaction conditions: (○) 250°C, 40 bar; (●) 250°C, 80 bar; (■) 250°C, 120 bar; (□) 300°C, 120 bar.

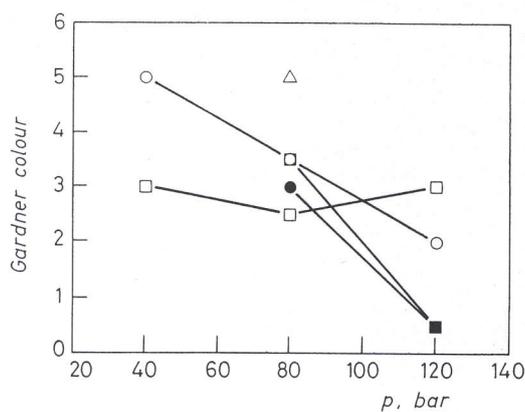
increased, and it was always higher when toluene was used as solvent. The influence of operating conditions on Gardner colour was not so clear. Increasing pressure yielded lower Gardner indexes, except for operation at 250°C with solvent-naphtha. Optimal temperature was a function of the pressure, being 250°C for 40 and 80 bar, and 300°C for 120 bar, in all cases with solvent-naphtha. The highest decoloration was obtained with toluene as solvent and reaction conditions of 120 bar and 300°C.

Catalytic hydrogenation affects the solvent-naphtha. Indene and coumarone present in the solvent were hydrogenated, but never completely (Fig. 3). If the behaviour of both compounds were similar when bonded to the polymeric resin chain, it would not be possible to saturate completely the resin, as was shown experimentally. Styrene was not affected, while benzonitrile disappears almost completely, giving toluene and ammonia as degradation products (both compounds were detected in the treated solvent-naphtha). Neither sulphur-containing components in the solvent-naphtha, nor hydrogen sulphide in the gas after reaction were detected.

The change of catalytic activity with time, an important factor in the economy of the industrial process, was studied in a series of experiments. The same catalyst sample was used in seven successive batch hydrogenation



(a)



(b)

Fig. 2. Colour (a) and saturation (b) of indene-coumarone resins hydrogenated with 1.5 wt % catalyst E for 4 h, employing different reaction temperature and solvent: (Δ) 200°C, solvent-naphtha; (□) 250°C, solvent-naphtha; (○) 300°C, solvent-naphtha; (■) 250°C, toluene; (●) 300°C, toluene.

reactions, at 250°C and 120 bar. As catalyst E is a powder, difficult to handle, catalyst F (a nickel catalyst, supplied in an extruded form by the same company), was used. A 3% wt of catalyst was introduced into two static gaskets inside the reactor. After every run, and before

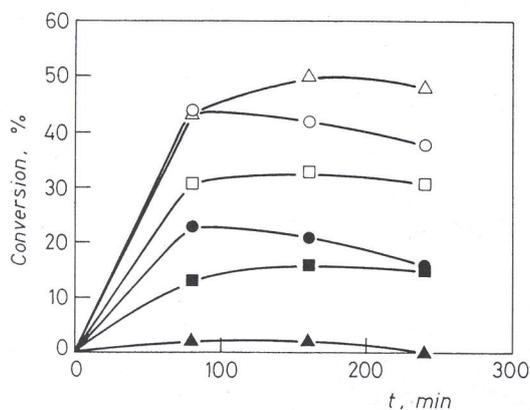


Fig. 3. Solvent-naphtha hydrogenation with 1.5 wt % catalyst E at 80 bar. Evolution of indene and coumarone conversion with time for different reaction temperatures: (Δ) indene, 200°C; (□) indene, 250°C; (○) indene, 300°C; (▲) coumarone, 200°C; (■) coumarone, 250°C; (○) coumarone, 300°C.

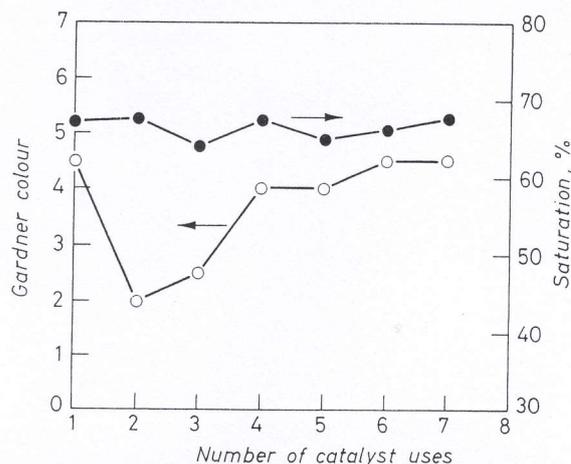


Fig. 4. Evolution of catalyst activity with successive uses. Indene-coumarone resins colour and saturation after hydrogenation with 3 wt % catalyst F (extrusions), at 250°C and 120 bar for 4 h, vs number of successive catalyst uses.

being reused, it was washed with toluene. Results are shown in Fig. 4. Resin saturation remained approximately constant in all experiments, while decoloration increased slightly in the first runs, decreasing later to a value close to the initial one. The catalyst did not lose activity appreciably in seven consecutive runs, for the conditions tested.

Two new catalysts, I and J, were also tested in the autoclave. Both are Shell nickel-molybdenum-on-alumina catalysts, in an extruded form. Before being used, the catalysts were presulphided with a mixture of 90% H₂-10% H₂S, at 50 bar and 350°C for 24 h. Tests were carried out at 80 and 120 bar and 200 to 300°C. No sulphur-containing compounds were added to the feed. Selected results are given in Table 2. Catalyst J yielded saturations higher than 50% for a temperature of 250°C or higher. However, Gardner colour decreased only slightly, the maximum decoloration being reached at 250°C and 80 bar. Catalyst I, similar to catalyst J, but with a smaller metal content, gave poorer results.

3.3 Stability of hydrogenated resins

Resins decolorated by catalytic hydrogenation tend to darken gradually. Colour evolution has been studied for resins dissolved in both solvent-naphtha and toluene, hydrogenated with catalyst E under different reaction conditions and a reaction time of 4 h. Hydrogenated resin solutions were kept in transparent glass flasks, and stored exposed to light. Samples were taken, and the Gardner colour was measured at different times, for a period of 30 days. The recoloration process was fast in the first few days, it being much slower in the final 15 days. Recoloration was severe. In some cases, the final Gardner colour was very close to the original value. There was a tendency to lower the Gardner colour after exposure by decreasing hydrogenation temperature and

TABLE 3

Evolution of Gardner Colour with Time for Hydrogenated Indene-Coumarone resins with Stabilizers Added (% in weight)

Stabilizer	Gardner colour after days			
	5	10	30	50
0.3 a+0.5 % d	5	10	11	12
0.3 % a	5	10	11	12
0.3 % b	4.5	9.5	10.5	12.5
0.3 % c+0.5 % e	6	10.5	11	12.5
0.3 % c	6.5	12	12	12.5
0.5 % d	9.5	10	10.5	12
0.5 % e	4	7.5	9	10
0.5 % f	5	9.5	10	11
0.5 % g	5	9.5	10	10.5
0.3 % a+0.3 % c	7.5	12	12	12.5
0.5 % g+0.5 % e	6	10	10.5	12
No stabilizer	4	9	10.5	12

Symbol Product and proposed mechanism of stabilization

^a Tinuvin 622 LD (Ciba-Geigy), radical chain breaking.^{3,16,17}

^b Tinuvin 770 DF (Ciba-Geigy), radical chain breaking.^{3,16,17}

^c Chimassorb 944 LD (Ciba-Geigy), radical chain breaking.^{3,16,17}

^d 2,2,6,6-Tetramethylpiperidine (Fluka), radical chain breaking.³

^e Phenylsalicylate (Fluka), UV adsorption.¹⁸

^f Diphenylamine (Merck), O₂ quenching.¹⁹

^g Di(tert-butyl)paracresol (Peroxid-Chemie), radical chain breaking.^{5,20}

increasing hydrogenation pressure. These factors were more important than Gardner colour measured immediately after hydrogenation. The lowest Gardner colour after 30 days was obtained for resin hydrogenated in toluene at 120 bar and 250°C.

In order to improve colour stability of hydrogenated resins, the addition of chemical stabilizers to the resin was tested. Resin dissolved in 50 wt% toluene (initial Gardner colour 15) was hydrogenated with 3 wt% catalyst E in powder at 250°C and 80 bar for 8 h. The Gardner colour of the product was lower than 1. The influence of stabilizers on recolouring prevention was tested with eleven compositions of seven stabilizers by addition to decolorated resin. Samples were kept in polyethylene transparent flasks, outdoors and protected from direct sunlight. Colour evolution for a period of 50 days was measured. Stabilizers tested and colour evolution data are given in Table 3.

Additives a, b, c and d showed no colour stabilization. All of them are piperidine derivatives, and they act by a non-consuming radical chain breaking mechanism. Additive g, a cresol derivative acts via a different consuming radical chain-breaking mechanism, and showed a slight colour stabilization. Additives e and f act mainly via UV adsorption and ¹O₂ quenching, respectively.

4 CONCLUSIONS AND PROCESS IMPLICATIONS

The first conclusion concerns the analytical methods. Iodine index, measured by both Wijs' and Hanus' methods, does not provide a reliable measure of indene-coumarone resin unsaturation. Iodine index, measured in very controlled conditions, may indicate a relative degree of unsaturation. Iodine index does not correlate always with the Gardner colour scale.

A high degree of resin decoloration can be reached by catalytic hydrogenation at high pressure and temperature. Best results were obtained with catalyst G-49-BRS (Ni-on-kieselguhr, Süd-Chemie), at 250–300°C and 80–120 bar. The nature of the solvent has an influence on the process: higher decolorations were attained when resin is dissolved in toluene instead of solvent-naphtha.

Decolorated resins are not stable, and tend to recolor. Recoloration tends to be lower for hydrogenation at low temperatures and high pressures. Resin redarkening was only slightly affected by the addition of the stabilizers tested. This behaviour can be explained by the impossibility of the total elimination of unsaturation by catalytic hydrogenation. Residual unsaturation remaining after hydrogenation allows the development of the recoloration process, favoured by the aromatic structure of the product. Unpolymerized indene and coumarone present in the solvent-naphtha, show a similar behaviour, and saturation is not completely reached.

In order to obtain clear stable resins, it is probably necessary either to eliminate residual unsaturation after hydrogenation, or to stabilize decolorated resins by adding appropriate additives. Further research is necessary in this area.

Solvent composition and processing temperature are factors that affect resin colour and stability. It is important to keep the temperature as low as possible throughout the entire resin manufacturing process, i.e. during the resin-solvent-naphtha separation by distillation, in order to get uncoloured resins.

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