Copolymerization of Turkish Tall Oil Specimens with Indene–Coumarone. II. Production and Properties of Indene–Coumarone Modified Tall Oil Varnishes

GÜLDEM ÜSTÜN[1,*] and HALİDUN CİVELEKOĞLU[2]

[1]Ege University, Engineering Faculty, Chemical Engineering Department, Bornova, Izmir, Turkey, and [2]Istanbul Technical University, Chemistry-Metalurgy Faculty, Chemical Engineering Department, Istanbul, Turkey

SYNOPSIS

Two varieties of tall oil were copolymerized with indene–coumarone and subsequently esterified with ethylene glycol, glycerol, and pentaerythritol in addition to these esters, Urethanes were also obtained by reacting pentaerythritol esters of copolymers with toluene diisocyanate (TDI). These resultant products were evaluated as varnish vehicles and their film properties were compared with some standard formulation of tall-oil- and vegetable-oil-based varnishes. The effect of indene–coumarone content of copolymer on the film properties of final products were additionally studied. Film evaluation showed that these copolymer-based varnish vehicles could be used in the field of organic surface coating.

INTRODUCTION

The tall oil is an accepted and important raw material for the paint and varnish industry. Since tall oil is a mixture of free fatty and resin acids rather than ester, it is not strictly analogous to common vegetable drying oils such as linseed or soybean oil. It must be modified to make it suitable for drying oil applications. These modifications can be accomplished by blowing, liming, esterification with polyhydric alcohols, or formation of tall oil modified alkyd resins.[1]

The tall oil esters, in particular, glycerol and pentaeriythritol esters, although in some cases with slower rate of drying and inferior durability, have been proposed as a useful substitute for inexpensive drying oils.[2–4] In the literature various ways of modification for improving or changing the properties and durability of tall oil esters have been also mentioned. The most common of these appear to be dilution of the tall oil esters with vegetable oils,[5] the addition of phenolic resin to the esters,[6] treatment of esters with toluene diisocyanate,[7] or treatment of tall oil with an unsaturated monomeric hydrocarbon such as styrene, cyclopentadiene before esterification.[8–10]

Another interesting modification of tall oil before esterification might be treatment with styrenelike monomers indene and coumarone, which are commercially available in Turkey. In the literature there is not any record concerning indene–coumarone modified tall oil or its related products. Therefore, in our previous investigation,[11] studies were conducted on the copolymerization of Dalaman and Çaycuma tall oil specimens with indene–coumarone and new types of tall oil copolymers were synthesized for the first time.

In this study, esters of these copolymers with ethylene glycol, glycerol, and pentaerythritol and the corresponding urethanes of these pentaerythritol esters were subsequently prepared. In order to compare these mentioned varnish vehicles with some standard formulation of organic surface coatings, tall-oil- and vegetable-oil-based vehicles were also included with these products. Consequently, film properties of oil products were investigated. Thus certain properties added to the products by introducing indene–coumarone in the main structure of tall oil are intensified at the same time.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 43, 1969–1975 (1991)
 CCC 0021-8995/92/111969-07$04.00

EXPERIMENTAL

Indene–coumarone copolymers of both Dalaman and Çaycuma tall oil samples, properties given in Table I, were preparatively obtained by applying the optimal conditions of 240°C and 16 h, taking the reactant ratio of tall oil to indene–coumarone 73 : 27, by mass, for Dalaman and 74 : 26 for Çaycuma samples.[11] Copolymer-based products and some standard commercial vehicles were prepared according to following procedures:

Preparation of Copolymer-Based Esters

Ethylene glycol, glycerol, and pentaerythritol esters of copolymers were prepared under the same working conditions as those of corresponding tall oil esters,[12–14] as follows: The esterification between polyhydric alcohol and copolymer was conducted in a 1-L round-bottom flask fitted with an inert gas connection, thermometer, stirrer, reflux condenser, and heating mantel. A constant flow of water having temperature of 95°C was supplied through the jacket of the reflux condenser so that the water formed during esterification would pass on through, whereas the polyhydric alcohol would be refluxed.

Copolymer and polyhydric alcohol 10% in excess of that calculated to give a zero acid number were placed in a reactor. Temperature was raised to previously established reaction temperature (240°C for ethylene glycol,[12] 275°C for glycerol,[13] and 290°C for pentaerythritol[14]) within 2 h and held for an acid number of 5–10. Throughout the reaction period, samples were taken at periodic intervals and the acid number of these samples were determined.

Preparation of Copolymer-Based Urethanes

In this process, pentaerythritol esters of copolymers were reacted with TDI (toluen diisocyanate consisting of 80% of 2, 4-, and 20% of 2, 6- isomers) according to the same working conditions of those corresponding tall oil urethanes set down by Culemeyer.[7]

The amount of TDI to be used was calculated as the equivalent amount of the free hydroxyl and carboxyl groups content of the esters.[15] The reaction was conducted in a four-necked flask equipped with a stirrer, thermometer, capillary glass tube for inert gas feeding, and air condenser. Pentaerythritol ester of copolymer was first taken into the flask and temperature was raised to 120°C. At this temperature TDI was added in small portions during 20 min. Following this addition, although the temperature showed a definite tendency to rise, it was kept at about 120°C until the free isocyanate value of content dropped down to 0.5%. Throughout the reaction period, samples were taken at definite time intervals and free isocyanate content of these samples was determined.[16]

Preparation of Tall-Oil- and Vegetable-Oil-Based Vehicles

In order to compare the new products mentioned above with some standard formulation of organic coatings, the following samples have been prepared:

- —boiled linseed oil,
- —boiled linseed: tung oil mixture (90 : 10, by mass),
- —linseed-oil-modified long oil alkyd resin,
- —ethylene glycol, glycerol, and pentaerythritol esters of tall oils,
- —urethanes of pentaerythritol esters of tall oils.

To obtain boiled oil samples, the oils were heated in a four-necked flask fitted with stirrer under nitrogen atmosphere for 8 h at 280°C.[17]

The standard fusion method[18] was applied to the preparation of linseed-oil-modified long oil alkyd resin.

The above-cited esters and urethanes of both Dalaman and Çaycuma tall oil specimens were prepared under the same working conditions applied to copolymers.

Determination of the Film Properties of Varnish Vehicles

Resin solutions were first prepared by diluting 50% of each product with mineral spirit (test benzin), by mass, and their some physical properties determined. Results are given in Table II.

As in seen from the data in Table II, some products were much more viscous than the others. In order to adjust the viscosity of samples in magnitude to 30–35 cp (20°C), varnishes were then prepared by diluting with an amount of mineral spirit sufficient to give a viscosity of 30–35 cp, the corresponding nonvolatile portion amounted to 30, 40, 50, and 60% of the total for the urethanes, pentaerythritol esters, alkyd resin, and the others, respectively, by mass. Naphthenate driers were added to provide 0.5% lead and 0.05% cobalt based on varnish solids.

For the determination of the drying time, varnish films were applied to glass strips using a Bird film applicator to give a film thickness of 40 μm, and left to dry in a dust-free room of 25°C temperature and of 55% relative humidity. Set-to-touch time and

Table I Properties of Indene–Coumarone Copolymers of Dalaman and Çaycuma Tall Oils

	Dalaman Copolymer	Çaycuma Copolymer
Dien value	11.53	10.77
Acid value	127.77	116.93
Indene–coumarone content (%)	20.78	19.75
Composition of tall oil:		
Fatty acids (%)	24.8	37.0
Resin acids (%)	73.4	58.0
Unsaponifiables (%)	1.8	5.0

hard-tack-free time were determined according to ASTM D 1640 and DIN 53150, respectively. The results are shown in Table III.

Alkali, water, and acid resistance tests were all performed according to ASTM D 1647-70. These tests were conducted at a temperature of 25°C, with aqueous solutions of 5% NaOH and 9% H_2SO_4 for alkali and acid resistance tests, respectively. Films were applied to a test tube by dipping it into the varnish, inversing it, and allowing it to dry. The test tube was then placed in a beaker containing solution. At periodic intervals the tubes were removed, rinsed with cold water, and the film examined. Time to failure of the film was noted.

Adhesion and flexibility tests were conducted according to ASTM D 3359-74 and DIN 53152, respectively. Hardness of the films was determined according to lead pencil method.[19] Film properties of these varnish films are presented in Table IV.

Water absorbency of films were determined according to Kaufmann and Brünning's method.[20] In this method, film of 40 μm thickness was applied to 5 × 7 × 0.2 cm glass plate and allowed to dry until constant weight was obtained. The plate was then submerged in water. At periodic intervals, the plate was removed, dried with adsorbent paper, and weighed. Water absorbency of film was calculated in an absorbed amount of water per unit mass of varnish. By plotting the percentage of the absorbed amount of water versus time, the water absorption curves of samples were obtained (Fig. 1).

Table II Some Physical Properties of the Prepared Products

	Product	Viscosity (20°C, cP)	Refractive Index (20°C)	Density (20°C, g/mL)	Color (Gardner)
Esters and urethane made from Dalaman copolymer	Ethylene glycol	10.63	1.4832	0.8890	18
	Glycerol	17.56	1.4842	0.8985	18
	Pentaerythritol	57.04	1.4858	0.9119	18
	Urethane[a]	46.52	1.4786	0.8744	18
Esters and urethane made from Çaycuma copolymer	Ethylene glycol	8.96	1.4828	0.8848	18
	Glycerol	16.74	1.4840	0.8939	18
	Pentaerythritol	40.80	1.4856	0.9070	18
	Urethane[a]	37.87	1.4764	0.8720	18
Esters and urethane made from Dalaman tall oil	Ethylene glycol	22.45	1.4834	0.8907	18
	Glycerol	31.67	1.4840	0.9014	18
	Pentaerythritol	78.93	1.4862	0.9279	18
	Urethane[a]	57.53	1.4742	0.8657	18
Esters and urethane made from Çaycuma tall oil	Ethylene glycol	15.33	1.4831	0.8860	18
	Glycerol	26.40	1.4852	0.8979	18
	Pentaerythritol	61.63	1.4859	0.9177	18
	Urethane[a]	46.05	1.4716	0.8633	18
Standard coating vehicles	Boiled linseed oil	16.86	1.4563	0.8269	13
	Boiled linseed: tung oil (90 : 10, by mass)	19.52	1.4568	0.8414	13
	Long oil alkyd resin	29.61	1.4622	0.8725	12

[a] As 40% solution in mineral spirit.

Table III Drying Time of the Prepared Varnish Vehicles

	Product	Set-to-Touch	Hard-Tack-Free
Esters and urethane made from Dalaman copolymer	Ethylene glycol	40 min	10 h
	Glycerol	27 min	8 h 50 min
	Pentaerythritol	17 min	8 h 25 min
	Urethane	8 min	23 min
Esters and urethane made from Çaycuma copolymer	Ethylene glycol	63 min	10 h 55 min
	Glycerol	40 min	9 h 15 min
	Pentaerythritol	33 min	8 h 40 min
	Urethane	15 min	35 min
Esters and urethane made from Dalaman tall oil	Ethylene glycol	54 min	13 h 35 min
	Glycerol	45 min	12 h 40 min
	Pentaerythritol	29 min	11 h 10 min
	Urethane	12 min	35 min
Esters and urethane made from Çaycuma tall oil	Ethylene glycol	70 min	13 h 50 min
	Glycerol	62 min	13 h 10 min
	Pentaerythritol	53 min	11 h 50 min
	Urethane	22 min	42 min
Standard coating vehicles	Boiled linseed oil	1 h 45 min	6 h 40 min
	Boiled linseed : tung oil (90 : 10, by mass)	1 h 25 min	6 h
	Long oil alkyd resin	1 h 10 min	6 h 10 min

Table IV Film Properties of the Prepared Varnish Vehicles[a]

	Product	Adhesion	Alkali Resistance	Water Resistance	Acid Resistance	Hardness	Flexibility
Esters and urethane made from Dalaman copolymer	Ethylene glycol	4B	NC	NC	NC	3H	P: 4 mm (+)
	Glycerol	3B	NC	NC	NC	2H	P: 6 mm (+)
	Pentaerythritol	3B–2B	NC	NC	NC	2H	P: 5 mm (+)
	Urethane	2B	NC	NC	NC	H	P: 8 mm (+)
Esters and urethane made from Çaycuma copolymer	Ethylene glycol	5B–4B	NC	NC	NC	3H	P: 3 mm (+)
	Glycerol	4B	NC	NC	NC	2H	P: 4 mm (+)
	Pentaerythritol	4B–3B	NC	NC	NC	3H	P: 3 mm (+)
	Urethane	3B	NC	NC	NC	H	P: 6 mm (+)
Esters and urethane made from Dalaman tall oil	Ethylene glycol	4B–3B	NC	NC	NC	5H	P: 5 mm (+)
	Glycerol	3B–2B	NC	NC	NC	4H	P: 6 mm (+)
	Pentaerythritol	2B	NC	NC	NC	H	P: 8 mm (+)
	Urethane	2B–1B	NC	NC	NC	HB	P: 10 mm (+)
Esters and urethane made from Çaycuma tall oil	Ethylene glycol	4B	NC	NC	NC	4H	P: 4 mm (+)
	Glycerol	4B–3B	NC	NC	NC	4H	P: 4 mm (+)
	Pentaerythritol	3B–2B	NC	NC	NC	2H	P: 6 mm (+)
	Urethane	3B–2B	NC	NC	NC	H	P: 8 mm (+)
Standard coating vehicles	Boiled linseed oil	5B	cp: 25 min	w: 45 min	NC	3H	P: 2 mm (+)
	Boiled linseed : tung oil (90 : 10, by mass)	5B	cp: 25 min	w: 13 min	NC	3H	P: 2 mm (+)
	Long oil alkyd resin	5B	pp: 10 min	w: 27 min	NC	4H	P: 2 mm (+)

[a] cp = complete peeling, pp = partial peeling, NC = no change, W = whitening appears in minutes and does not disappear within 24 h, and P = passed by bending over a certain diameter of mandrel.

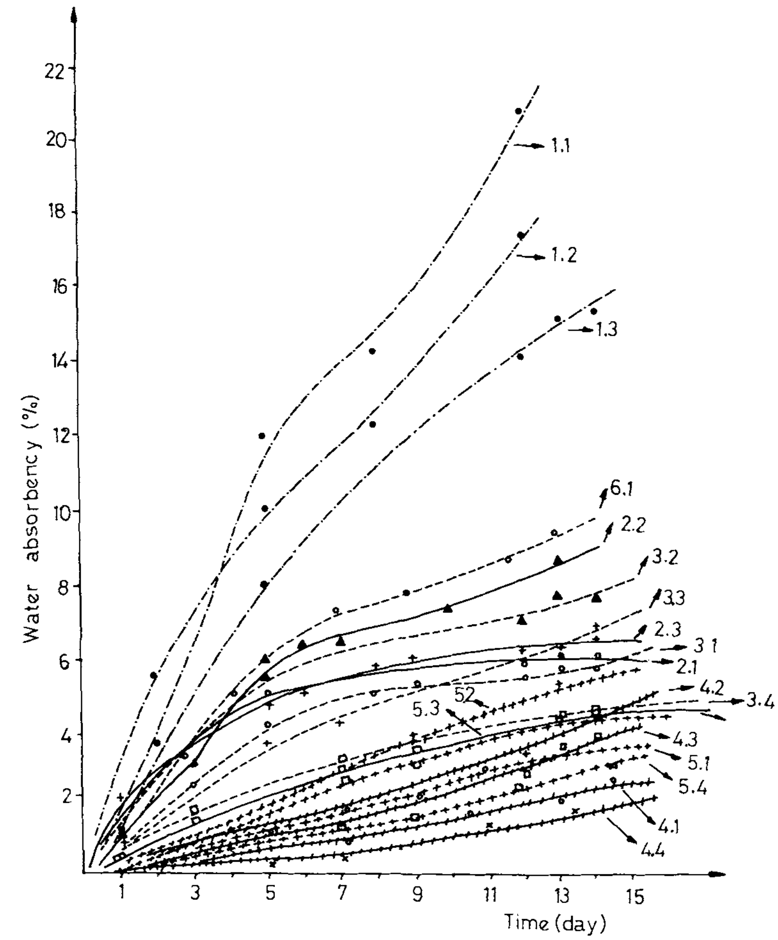

Figure 1 Water absorbency curves of all products. (1) Standard coating vehicles: (1.1) boiled linseed: tung oil; (1.2) boiled linseed oil; (1.3) long oil alkyd resin. (2) Dalaman-copolymer-based: (2.1) ethylene glycol ester; (2.2) glycerol ester; (2.3) pentaerythritol ester; (2.4) urethane. (3) Çaycuma-copolymer-based: (3.1) ethylene glycol ester; (3.2) glycerol ester; (3.3) pentaerythritol ester; (3.4) urethane. (4) Dalaman-tall-oil-based: (4.1) ethylene glycol ester; (4.2) glycerol ester; (4.3) pentaerythritol ester; (4.4) urethane. (5) Çaycuma-tall-oil-based: (5.1) ethylene glycol ester; (5.2) glycerol ester; (5.3) pentaerythritol ester; (5.4) urethane. (6) Çaycuma copolymer (having 20.11% indene–coumarone) based ethylene glycol ester.

RESULTS AND DISCUSSION

In the present work indene–coumarone copolymers of Dalaman and Çaycuma tall oil samples, properties given in Table I, were evaluated as substitute drying oils for cheaper grade of varnish. For this purpose esters of these copolymers with ethylene glycol, glycerol, pentaerythritol, and the corresponding urethanes of pentaerythritol esters were prepared, made into varnishes, and evaluated for film properties.

Properties of the copolymer based esters and urethanes in comparison with tall oil and vegetable based vehicles are given in Tables II–IV. Water absorbency of all products is shown in Figure 1.

Evaluation of data concerning the film and water absorbency properties indicated that all the copolymer-based products showed superior alkali and water resistance and excellent water absorbency in comparison with the vegetable-oil-based products. But their drying, adhesion, and flexibility properties were to a minor extent not as good as the oil-based products.

On the other hand, it was experimentally observed that copolymer-based products were drying at an appreciably faster rate and producing more flexible and less brittle films than those of the cor-

Table V Film Properties of Ethylene Glycol Esters Derived from Çaycuma Copolymers Containing Different Amounts of Indene–Coumarone

Tests	Ethylene Glycol Ester of Copolymer: Containing 19.75% Indene–Coumarone	Ethylene Glycol Ester of Copolymer: Containing 22.11% Indene–Coumarone
Drying time:		
Set-to-touch	63 min	49 min
Hard-tack-free	10 h 55 min	10 h 05 min
Water resistance	NC	NC
Alkaline resistance	NC	NC
Acid resistance	NC	NC
Adhesion	5B–4B	5B
Flexibility	P: 3 mm (+)	P: 2 mm (+)
Hardness	3H	3H

responding tall-oil-based products. Addition of indene–coumarone to tall oil may result in reduction of brittleness and improvement in the quality of the film. These results were in agreement with those of literature reports for other sorts of indene copolymers.[21]

It was also found that film properties were closely related to the composition of tall oil. In an examination of the film properties of two grades of tall oil products, Dalaman and Çaycuma, containing, respectively, 73 and 58% resin acids, it was shown that the resin acid content influenced considerably drying, adhesion, and flexibility properties. The varnishes prepared from Dalaman tall oil, having relatively high resin acid content, have better drying properties and poorer adhesive and flexibility properties than varnishes from Çaycuma tall oil of lower resin acid content. This also confirms the literature reports cited for other tall oil varnishes.[1,8] Water absorbency properties of same products were roughly equal in this respect.

Through evaluation of Tables III and IV, it was concluded that the drying properties of TDI-modified esters were superior to those of other products. But, with respect to adhesion and flexibility properties, the addition of TDI had a negative effect on these properties. This confirms the practical approach cited in the literature[15] as "the presence of TDI in surface coatings leads to a decrease of adhesion and flexibility properties."

Among the all-copolymer-based products, the ethylene glycol ester of Çaycuma copolymer was the only product which had acceptable adhesion and flexibility; however, this ester exhibited longer drying time than the others. As stated above, improvements in drying ability, adhesion, and flexibility were significantly observed in all the indene–coumarone-modified tall oil products when compared to the corresponding unmodified tall oil products. In order to improve drying ability of this ester, the indene–coumarone content of Çaycuma copolymer was increased and previous experiments were repeated with the sample of this copolymer having high indene–coumarone content as follows:

At first, the new sample of Çaycuma copolymer was prepared by applying the optimal conditions of 240°C and 16 h, taking the new reactant ratio of tall oil to indene–coumarone 59 : 41, by mass. By this treatment, the indene–coumarone content of copolymer was increased from 19.75 to 22.11%. Subsequently, ethylene glycol ester of this copolymer was obtained, made into varnish, and evaluated for film properties under the same working conditions. Film test results are shown in Table V. The graphical representation of the water absorbency results is also plotted in Figure 1.

As expected, the results showed that the drying time, adhesion and flexibility of ethylene glycol varnish film were considerably improved with increased indene–coumarone content. But its water absorbency was slightly decreased.

As a conclusion, indene–coumarone-modified tall oil varnishes having acceptable film properties could be obtained from tall oil, particularly having low resin acid content, and used in the field of organic surface coating.

There is a steadily increasing need for such low-cost and durable organic surface coatings based on industrial byproducts, particularly in Turkey, and it is believed that surface coatings formulated with indene–coumarone copolymers of tall oil would fill this need to some extent. This investigation of these new products may contribute much toward justifying this thesis.

REFERENCES

1. P. D. Patrick, M. G. Bestul, and R. W. Gressang, *Tappi,* **36,** 561–564 (1953).
2. D. L. Emerson, *Paint Oil Chem. Rev., Nov. 24,* 13–14, 26–27, 30–32 (1949).
3. W. Brushwell, *Am. Paint J.,* **38,** 80–86 (1955).
4. K. Berger, *Plaste Kautschuk,* **10,** 566–568 (1963).
5. R. Hastings, *Am. Paint J.,* **28,** 42, 46, 48, 50 (1943).
6. B. Widegren, *Tek. Tidskr.,* **74,** 153–158 (1944).
7. C. Culemeyer, U.S. Pat. 2,812,337 (1957).
8. D. W. Bosch and R. B. Drubel, *Oil Paint Drug Rep.,* **160,** 85 (1951); *Paint Oil Chem. Rev.,* **114,** 80–86 (1951).
9. H. Beduneau, *Rev. Chim. Prod.,* **55,** 1–3 (1952).
10. Jr. R. Priester, *Seifen Öle Fette Wachse,* **101,** 80–81 (1975).
11. G. Üstün and H. Civelekoğlu, *J. Appl. Polym. Sci.,* to appear.
12. L. G. Zachary, H. W. Basak, and F. J. Eveline, Eds., *Tall Oil and Its Uses,* McGraw-Hill, New York, 1965.
13. R. S. Aries and H. Wolkstein, *Tappi,* **38,** 691–696 (1955).
14. E. R. Mueller, P. L. Eness, and E. E. McSweeney, *Ind. Eng. Chem.,* **42,** 1532–1536 (1950).
15. J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology, II—Technology,* Wiley-Interscience, New York, 1964, Part II, pp. 453–607.
16. S. Siggia and J. G. Hanna, *Anal. Chem.,* **20,** 1084 (1948).
17. *Ullmanns Encyklopaedie der technischen Chemie, 3. Auflage,* München, 1966, Band 17, pp. 727–728.
18. H. Civelekoğlu, R. Tolun, et al., *Sinai Kimya Öğrenci Laboratuvari Çalişma Yönergeleri,* İTÜ Kimya-Metalurji Fak., Istanbul, 1982, p. 14.
19. B. Zeidler, *Laboratoriumsbuch für die Lack and Anstrichmittel-Industrie III. Auflage,* Wilhelm Knapp Verlag, Düsseldorf, 1967, p. 298.
20. H. P. Kaufmann and H. Brünning, *Fette Seifen Anstrichmittel,* **62,** 1146–1152 (1960).
21. Revertex Ltd., Fr. Pat. 1,359,184 (1964).

Received March 28, 1990
Accepted January 9, 1991