Konya Mühendislik Bilimleri Dergisi, c. 13, s. 1, 307-320, 2025
Konya Journal of Engineering Sciences, v. 13, n. 1, 307-320, 2025
ISSN: 2667-8055 (Electronic)
DOI: 10.36306/konjes.1586565

URETHANE-MODIFIED ALKYD RESIN BASED PAINT PRODUCTION: DETERMINATION OF PAINT PROPERTIES

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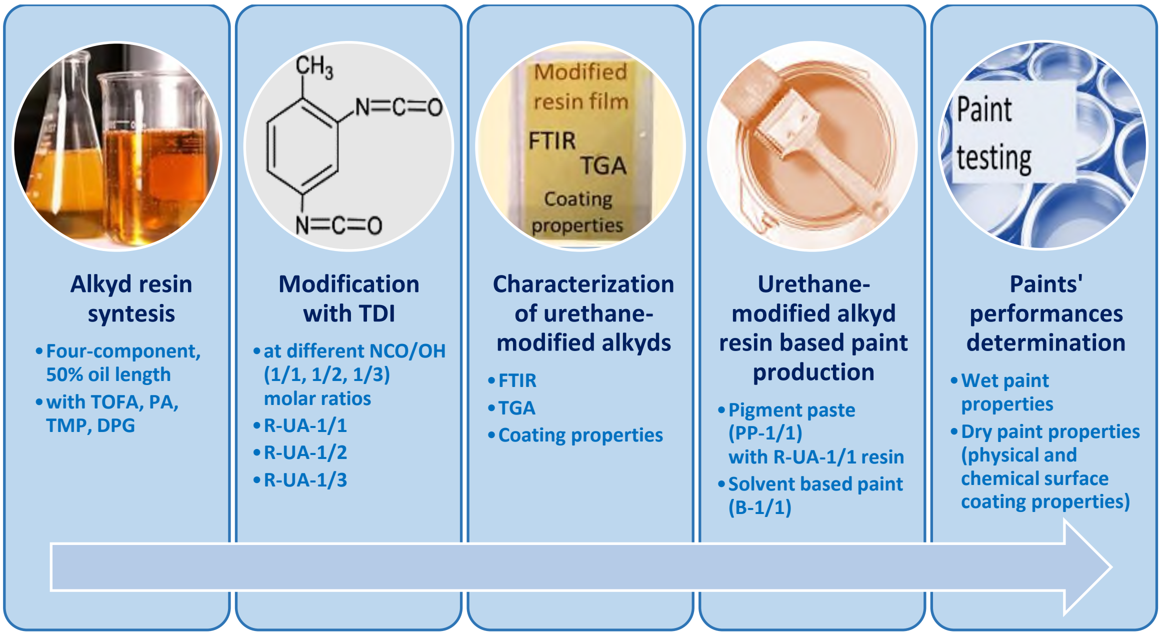
Highlights

- Urethane-modified alkyds were prepared at NCO/OH molar ratios of 1/1, 1/2, and 1/3 using TOFA-alkyd with a 50% oil length and TDI.
- Good physical/chemical coating and good thermal properties were observed in modified alkyds.
- A stable paint system was created successfully using the best resin (NCO/OH mole ratio: 1/1) as a binder in solvent-based paint.
- The wet paint properties of urethane-modified alkyd-based paint were quite suitable for production.
- The paint films exhibited high abrasion resistance, superior adhesion strength, excellent environmental resistance, gloss, and high resistance to acid, water, and household chemicals.

Graphical Abstract



Flowchart of this study

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(Received: 16.11.2024; Accepted in Revised Form: 17.02.2025)

ABSTRACT: Alkyd resins have an important place among the binders used in the paint industry. One of the major advantages of alkyd resins is that they are susceptible to various modifications to gain the desired properties. In this study, urethane-modified alkyd resins were synthesized at different modification ratios using toluene diisocyanate as a modifier. The resin with the determined optimum modification ratio was used as the binder resin in the paint formulation. In the synthesis of four-component alkyd resin with 50% oil length, phthalic anhydride, tall oil fatty acid, trimethylolpropane, and dipropylene glycol were used. The synthesis of urethane-modified alkyd resins (R-UA-1/1, R-UA-1/2, and R-UA-1/3) was carried out by modification reactions of the prepared alkyd resin with TDI at different NCO/OH (1/1, 1/2, 1/3) molar ratios. Characterization of modified resins was performed by Fourier transform infrared spectroscopy. Subsequently, the optimum NCO/OH ratio was determined due to the physical and chemical surface coating properties and thermogravimetric analysis results of the resin films. The best results were obtained in the resin, where the modification ratio was NCO/OH: 1/1. Then, the urethane-modified alkyd resin (R-UA-1/1) prepared in this ratio was used as a binder in the solvent-based paint formulation. The wet/dry paint properties and household chemical resistance properties of solvent-based paint (B-1/1), prepared using urethane-modified alkyd resin, were examined with tests according to the standards, and the coating performance of this paint was determined in detail. As a result, durable coatings that are suitable for interior applications and can compete with alkyd paints were obtained from the paint prepared with urethane-modified alkyd resin.

Keywords: *Alkyd, Coating Properties, Modification, Synthetic Paint, Urethane-Modified Alkyd Resin, Wet/Dry Paint Properties*

1. INTRODUCTION

In recent times, there has been a rapid increase in industrialization and improvements in the global economy, leading to a rise in production and demand in the paint industry. Since coating/paint products provide resources to a wide area, especially the construction and manufacturing industry, the paint sector significantly affects other sectors and is affected by all sectors. The paint sector has a wide range of products that address many areas such as interior, exterior, marine, automobile, furniture, heavy industry, road-marking, and heat-resistant paints. In this context, the performance of the paint should be appropriate for the intended application area, ensuring durability and long life, while also being cost-effective and easy to apply. The most crucial component that offers various properties to the paint according to its usage area and determines its performance is the binder resin, which constitutes the majority of the paint's composition. In paint formulations, mostly alkyd, polyester, polyurethane, epoxy, silicone, acrylic, etc. resins are used as binder resins.

Alkyd resins are products of the condensation reaction of polyacids, polyols, and monofunctional fatty acids or oils. They are suitable for producing coating materials due to their compatibility with most polymers and wide formulation choices. Alkyds are mostly preferred as binders in surface coatings such

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as paints and varnishes that form a hard and continuous film [1], [2]. It can be modified with various chemicals to gain the desired properties for use in different areas [3]. Alkyd resin, which is frequently used as a binder in the paint industry, affects not only the physical properties of the paint, such as hardness, flexibility, abrasion, impact resistance, and gloss, but also its chemical properties, such as acid, alkali, water, and solvent resistance [4], [5]. In conclusion, alkyd resins hold a significant position among binders in the paint industry due to superior coating properties, favorable manufacturing conditions, cost-effective raw material prices, high storage stability, and adaptability for various modifications [6], [7], [8].

Urethane-modified alkyd resins (uralkyds), prepared by modifying alkyd resins with toluene diisocyanate (TDI), have advantages such as fast drying, high resistance to chemical factors, compatibility on various surfaces, formation of glossy films on wooden surfaces, and formation of hard/non-flexible films. At the present time, urethane alkyds have a wide range of applications as binders in construction paints and varnishes. Urethane-modified alkyd resins provide better abrasion and hydrolysis resistance than alkyd coatings [3]. There are studies in the literature on the use of various alkyd and modified alkyd resins as binders in paint formulations. Soybean oil-based alkyd resins [7] and acrylic-modified water-reducible alkyd resin [8] obtained from waste PET intermediates, modified alkyd resins based on a new source of dicarboxylic acid [9], indicum seed oil modified alkyd resin [10] were used as a binder in paint formulations.

In this study, urethane-modified alkyd resins were synthesized at various modification ratios using TDI as a modifier. Then, the modified alkyd resin, prepared at the optimum modification ratio, was used as a binder component in the paint formulation. For this, firstly, the surface coating properties of urethane-modified alkyd resins synthesized at various modification ratios were determined, and their thermal behaviors were examined by the TGA method. Then, the wet/dry paint properties and household chemical resistance properties of the solvent-based paint, prepared using the urethane-modified alkyd resin with optimum ratio, were examined with tests in accordance with the standards, and the coating performance of the prepared paint was determined.

2. MATERIAL AND METHODS

2.1. Materials

TOFA, used in alkyd resin synthesis, was supplied by Arizona Chemicals (USA). TMP and PA were provided by Perstorp (Sweden) and Sigma-Aldrich (USA), respectively. Toluene 2,4 diisocyanate (TDI), used in modification, is a Sigma-Aldrich product. Dispersion and wetting agent (DISPERBYK-108), used for paint systems, is a BYK (Germany) product. Bentone, used as additive, was supplied by Boysan Boya (Turkey). Titanium dioxide (TiO_2), butylglycol and soy lecithin were purchased by Sigma Aldrich. Pigment (Eisenoxydgelb 920) is a product of Bayer (Germany). Driers (cobalt naphthenate and manganese naphthenate as primary driers, 6% solution, zirconium naphthenate, and calcium naphthenate as auxiliary or secondary driers, 6% solution) were provided by Akpa Kimya (Turkey). Acetone, ethanol, methanol, xylene, toluene, and ethyl acetate, used in reactions and tests, are products of Merck (Germany). All other materials are of analytical or synthesis purity. Distilled water was used in all experimental studies.

2.2. Methods

2.2.1. Synthesis and characterization of urethane-modified alkyd resins

Alkyd resin formulation calculations were performed using the K alkyd constant system. Tall oil fatty acid (TOFA), phthalic anhydride (PA), trimethylolpropane (TMP), and dipropylene glycol (DPG) were used in the synthesis of a four-component, 50% oil-content alkyd resin. Afterward, urethane-modified alkyd resins were synthesized by the modification reactions of alkyd resin with TDI at various (NCO/OH: 1/1, 1/2, and 1/3) molar ratios. These modified resins were symbolized as "R-UA-1/1", "R-UA-1/2" and "R-UA-1/3", respectively.

The alkyd synthesis and urethane-modification reactions were carried out in the five-necked glass reactor in a heating mantle. In alkyd synthesis, the glass reactor was equipped with a mechanical stirrer, gas inlet, thermometer, reflux condenser + Dean-Stark part. On the other hand, in modification reactions, the reaction system included a mechanical stirrer, gas inlet, thermometer, and dropping funnel.

The modification reaction temperature was kept constant at around 40°C during the TDI addition. The progress of the reactions and the isocyanate group contents were followed by isocyanate determination (ASTM D 2572) of samples taken from the reactor at certain time intervals [3]. The structural characterizations of the synthesized urethane-modified alkyd resins were performed using Agilent brand Cary 630 model Fourier Transform Infrared Spectroscopy (FTIR).

2.2.2. Surface coating tests and thermal analyses of urethane-modified alkyd resins

The optimum NCO/OH ratio of the modified resins was determined according to their physical/chemical surface coating and thermal properties. The NCO/OH ratio in the resin that was best in terms of coating performance and thermal properties was specified as the optimum ratio.

The physical and chemical surface coating properties of the films prepared from modified resins were tested according to the related standards. Details about these tests are presented in the relevant section below.

Thermal properties of the modified resin films were investigated using the Linseis brand STA PT 1750 model Thermogravimetric Analysis (TGA) device. Samples (~10 mg) were prepared from oven-dried films. Measurements were carried out by heating from room temperature to 650^{o}C at a rate of 10^{o}C/min in air atmosphere.

2.2.3. Urethane-modified alkyd resin based paint production

Preparation of the solvent-based paint was carried out in two stages using a high-speed laboratory-type disperser (Yökeş brand VBR-12 model, Turkey). In the first stage, urethane-modified alkyd resin diluted to 65% (wt.) solids, pigment, and wetting agent were mixed homogeneously with low-speed mixing to prepare the pigment paste. In the second stage, after adding other paint components and additives to the prepared paint paste, the mixing speed was gradually increased and mixing was realized at the necessary speed (peripheral speed: ~20 m/s) for complete dispersion. Thus, a urethane-modified alkyd resin-based paint system was prepared by ensuring that the pigments were completely wetted by the binder.

2.2.4. Surface coating / paint tests applied to resins and paint

The surface coating properties of the synthesized resins and the wet/dry paint properties with the household chemicals resistances of the paint were determined by tests conducted according to standards.

2.2.4.1. Wet Paint Tests

The solids content% (ASTM-D 1259), density (with BYK density-cup, according to ISO 2811), viscosity (with Brookfield DV2T rotary viscometer, according to ASTM-D 2196), flow time (with BYK flow-cups, according to ISO 2431), particle size (with BYK grindometer, according to ASTM-D 1210-05) and hiding power property (with BYK Byko-charts, according to ISO 6504) were tested for determination of wet paint properties of prepared urethane-modified alkyd resin based synthetic paint.

Solids content: After weighing the paint in the petri dish, it was placed in the oven at 110°C and kept there until it reached a constant weight. The final weighing was then recorded. The solids content was calculated as a percentage based on the weighing measurements.

Density: The density of the paint was determined by filling the tared density-cup and weighing it again. The density was calculated based on the weighing measurements.

Viscosity: In a rotary viscometer, to determine dynamic viscosity values, measurement was taken when the torque value reached 50% of the appropriate speed set for the selected spindle, based on the viscosity value at room temperature (20-25^{o}C).

Flow time: The time taken for the flow-cup, which was 8 mm in orifice diameter and filled with paint, to empty with a continuous and uninterrupted paint flow at room temperature was determined in seconds.

Particle size: 1 mL of paint was dropped onto the deep edge of the grooves on the 100 μm grindometer, and the paint was spread along the grindometer using the applicator. The value corresponding to the point where the homogeneous image disappeared and dots began to appear in the paint film on the grindometer was determined as the particle size of the paint, and results were given in micron (μ) and Hegman (NS).

Hiding power: Hiding power cards (BYK, Byko-charts) cut into squares were weighed. The paint was applied with a brush to the card in such a way that the checkerboard pattern substrate was not visible and the card was weighed again. The hiding power value was calculated in g/cm^2 according to the first and final weighing of the cards with known surface area and weight.

2.2.4.2. Dry Paint / Surface Coating Tests

Dry paint / surface coating tests were carried out in two groups, and thus (I) Physical coating properties and (II) Chemical coating properties were determined.

(I) Physical coating properties

To determine the physical surface coating properties of resin films (50 μ) and the dry paint properties of the paint film (100 μ), "drying degree" (Erichsen 415/E drying-time tester), " pendulum hardness" (Sheen König pendulum), "adhesion strength" (Erichsen GS 10 cross-cut), "impact resistance" (BYK Gardner PF-1115 impact tester), "abrasion resistance" (Erichsen 2511-11 falling sand tester), and "gloss" (Sheen 101 N gloss meter) measurements were performed based on related standards.

Drying degree (DIN 53150): In this standard, the drying degree is performed according to the "Modified Bandow Wolf method". In this method, 7 drying degrees are defined between 1-7. The 1st drying degree is determined by whether the 0.2 mm diameter glass beads poured on the film adhered to the surface after 10 s. On the other hand, drying degrees between 2 and 6 are determined by whether the Kraft paper adhered to the film surface after applying 5, 50, 500 and 5000 g/cm^2 pressure for 60 s. In addition, the dry-to-touch stage (the paint does not stick to the finger when touched) of these films was also determined according to the ASTM D 1640 standard.

Pendulum hardness (DIN 53157): For the measurement, the film-coated glass plate is placed on the König pendulum. Then, the damping time of the pendulum oscillating in the specified amplitude (from 6^{o} to 3^{o}) is determined. The results are given in "König seconds".

Adhesion strength (ASTM D 3359-76): The film on the glass plate is cut at right angles with a cross-cut cutter to create a lattice pattern (6 x 6 = 36), and this pattern is swept with a brush. The appearance of the lattice pattern is compared with the standard, which is classified according to the amount of squares remaining intact. The results are given in "% adhesion".

Impact resistance (ASTM D 2794-69): The test is based on the principle of observing the deformation on the film surface as a result of dropping a standard cylindrical steel weight through a guide tube onto a film-coated metal plate. The results are determined as "kg x cm" according to the standard weight used and the height of the drop.

Abrasion resistance (ASTM D 968-05): First, a film-coated glass plate is placed at a 45^{o} angle in the device. The hard sand that passes through sieve no. 25 and remains in sieve no. 30 is allowed to pour freely onto the film surface via a vertical tube due to the gravity effect. The test continues until the volume of sand required to create a ~4 mm diameter erode gap on the film surface is reached. The results are reported as "mL sand".

Gloss (ASTM D 523): This test method is based on the principle of measuring the specular reflectance of light on the surface of the film-covered glass plate and comparing it with that of black glass. The results are expressed as "gloss unit (GU)".

(II) Chemical coating properties

To determine the chemical surface coating properties of the resin films (50 μ), water, acid, salt, alkali, solvent and environmental resistance tests, and for the chemical dry paint properties of the paint films (100 μ), household chemicals, solvent, and environmental resistance measurements were performed according to relevant standards/literature.

Water, acid, salt and alkali resistance (ASTM D 1647-89): The film-coated tin plate, prepared by casting method, was immersed in a beaker filled with distilled water at room temperature, and kept for 18 h. After 18 h, the plate was examined after being wiped dry, and 20 min, 1 h and 2 h later.

The film, prepared on the glass plate by the film applicator, was immersed in a beaker containing 3% (wt.) sulfuric acid (H_2SO_4), and the changes on the film surface were examined for 72 h.

The film prepared on the glass plate by the film applicator, was immersed in a beaker containing 5% (wt.) sodium chloride (NaCl), and the changes on the film surface were examined for 72 h.

The alkali resistance test was carried out using the films which prepared by immersion method on glass tubes. The films were immersed in beakers containing dilute sodium hydroxide (0.1 M NaOH) solution, and the changes on the surfaces of the films were examined for 72 h. Then, this test was repeated by immersing the films, which were resistant to dilute solution, in beakers containing concentrated NaOH solution (3% wt.)

***Solvent resistance** [11]:* 1x1 cm gauze pieces impregnated with methanol, toluene, ethyl acetate, and acetone were placed on the film surface of glass plate after removing excess solvent with filter paper and covered with Petri dishes. After 30 minutes, the Petri dishes were removed, and changes on the film surfaces were observed.

***Environmental resistance** [11]:* First, the film prepared on the glass plate was kept in a beaker containing distilled water at room temperature for 18 h, then in a deep freezer at -20±2ºC for 3 h, and then in an oven at 50±2°C for 3 h. At the end of all these stages, 1 cycle was completed, and the film was examined visually at the end of each cycle.

Household chemical resistance (ASTM-D 1308-02): In this tests applied to the dry paint film, 3% H_2SO_4 (wt.), 0.1 M NaOH, 3% NaOH (wt.), cold water (25°C), hot water (80°C), 8 g/L soft soap solution and 1 g/L dishwashing detergent solution were used to determine acid, alkali, distilled water, soap, and detergent resistances of the paint by the immersion method. According to the immersion method, paint-coated metal plates (or glass plates for distilled water resistance) were immersed in beakers containing the test solution at room conditions. Changes on the film surface were observed for 72 h.

Alcohol, vinegar, and beverage resistances were determined by spot test using 50% ethyl alcohol (v/v), 3% acetic acid by weight, 1 tea bag brewed for 5 min/100 mL distilled water, 2.5 g coffee/100 mL distilled water, and cola. According to the spot test method, 1 mL of test solution was dropped on the paint-coated metal plate and covered with a watch glass. Drops were wiped at certain intervals, and changes on the surface of the paint were observed.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis of Urethane-Modified Alkyd Resins

FTIR spectra of urethane-modified alkyd resins (R-UA-1/1, R-UA-1/2, R-UA-1/3) synthesized at different NCO/OH modification ratios are presented in Figure 1. As given in the literature, the FTIR spectrum of TDI has a sharp absorption peak at 2250 cm^{-1} belonging to the stretching vibration of the isocyanate (-N=C=O) group [3], [12], [13], [14]. When the spectra of urethane-modified alkyd resins in Figure 1 were examined, it was seen that this sharp peak belonging to the -N=C=O group of TDI was not observed in the resin spectra. This situation confirms that the -NCO groups of TDI and the free -OH groups [15], [16], [17] of the alkyd resin have completely reacted. In addition, the presence of characteristic peaks belonging to the urethane structure observed in the FTIR spectra of all modified resins (-NH stretching peak at 3355 cm^{-1} belonging to urethane bonds [14], [18], stretching vibration in 2850-3000 cm^{-1} region of the aliphatic C-H bond [15], [16], [17], [19], [20], the vibration of the carbonyl (-C=O) group at 1730 cm^{-1} belonging to the urethane bond [15], [16], [17], [18], [19], [20], -NH deformation peak at 1534 cm^{-1} [16], [17], -NH bending vibration at 1599 cm^{-1} [18], -CN stretching vibration in 1386-1278 cm^{-1} [20] region attributed to the amide II band) indicates the formation of urethane alkyd structure.

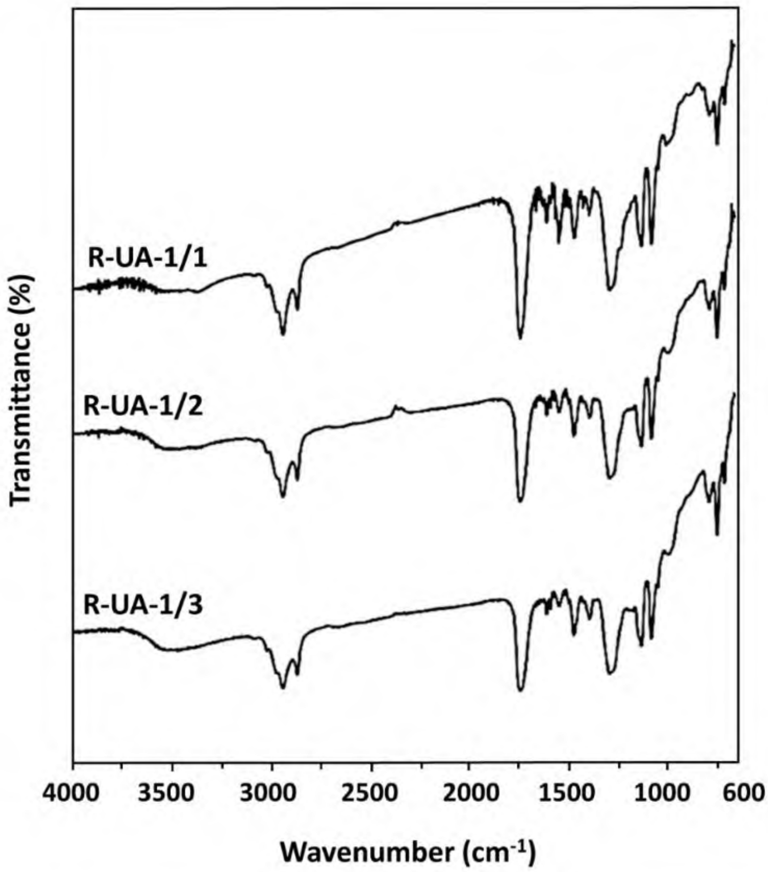

Figure 1. FTIR spectra of urethane-modified alkyd resins.

3.2. Surface Coating Properties of Urethane-Modified Alkyd Resins

Before physical and chemical surface coating tests for resins, driers were added to the diluted resin in proportion to 1% Zn and 0.1% Co by weight based on the amount of urethane-modified alkyd resin. Then, the resin films were prepared using the BYK film applicator (50 μ) for tests.

3.2.1. Physical surface coating properties

First of all, the drying degrees of the modified resin films were monitored in the air. By the end of 72 h, the films reached the 4th, 5th, and 6th drying degrees. Prior to testing their physical and chemical surface coating properties, the films were oven-cured at 110°C for 2 h. This process resulted in all films achieving the 7th drying degree, indicating that they were fully dried throughout their thickness according to the standard.

The physical surface coating test results of urethane-modified alkyd resin films, which were determined after oven-curing at 110°C for 2 h, are presented in Table 1.

Table 1. Physical surface coating properties of urethane-modified alkyd resin films.

Physical Coating Tests	**Urethane-Modified Alkyd Resins**		
	R-UA-1/1	**R-UA-1/2**	**R-UA-1/3**
Drying degree (in the air for 72 h)	6	5	4
Drying degree (at 110°C for 2 h)	7	7	7
Hardness (König second)	179	128	109
Adhesion strength (%)	100	100	100
Impact resistance (kg x cm)	200	100	75
Abrasion resistance (mL sand)	6000	5000	4000
Gloss (GU)	116	121	119

As seen in Table 1, hard and glossy films with excellent adhesion strength were obtained from the synthesized urethane-modified alkyd resins. Moreover, it is observed that hardness, abrasion, and impact resistance values increase with increasing NCO/OH ratio. Among the urethane-modified alkyd resins with different NCO/OH molar ratios, the best physical surface coating properties were observed in the resin with 1/1 NCO/OH ratio (R-UA-1/1) with hardness of 179 König seconds, abrasion resistance of 6000 mL sand, impact resistance of 200 kg x cm, and adhesion strength of 100%.

3.2.2. Chemical surface coating properties

The chemical surface coating test results of urethane-modified alkyd resin films, which were determined after oven-curing at 110°C for 2 h, are presented in Table 2.

As seen in Table 2, urethane-modified alkyd resin films have excellent acid, salt, water, solvent, and environmental resistance. However, the alkali resistances of these films varied according to the modification ratio (NCO/OH ratio). For example, R-UA-1/1 resin film was resistant to dilute alkali solution (0.1 M NaOH) for 72 h whereas R-UA-1/2 and R-UA-1/3 resin films were able to resist 6 and 3 h, respectively. For the R-UA-1/1 resin film, that was resistant to 0.1 M NaOH solution, the alkali resistance test was repeated with a concentrated alkali solution (3 wt.% NaOH). R-UA-1/1 resin film started to be affected by 3% NaOH solution after 24 h, and it was completely separated from the surface after 72 h. As can be seen from these results, the alkali resistance of alkyd resins known to have poor alkali resistance [21] was slightly increased with urethane modification. Especially, the alkali resistance of urethane-modified alkyd resin with an NCO/OH ratio of 1/1 is good according to the literature and can be improved further.

According to the physical and chemical surface coating test results of the resin films modified at different ratios, it was observed that the R-UA-1/1 resin with an NCO/OH molar ratio of 1/1 had the best coating performance.

3.3. Thermal Properties of Urethane-Modified Alkyd Resins

Thermogravimetric analyses were performed to determine the thermal properties of the urethane-modified alkyd resin films. The TGA curves obtained from the thermal analyses are presented comparatively in Figure 2.

As seen in Figure 2, the urethane-modified alkyd resins showed similar thermal behavior profiles. The final thermal oxidative decomposition temperatures of R-UA-1/1, R-UA-1/2, and R-UA-1/3 resins were found to be 506°C, 499°C, and 518°C, respectively, indicating their high thermal resistance.

According to the thermal analysis and all other surface coating test results, optimum results were obtained in the resin where the modification ratio was NCO/OH: 1/1. The urethane-modified alkyd resin (R-UA-1/1) prepared in this ratio was used as a binder in the solvent-based paint formulation.

Table 2. Chemical surface coating properties of urethane-modified alkyd resin films.

Chemical Coating Tests	Urethane-Modified Alkyd Resins		
	R-UA-1/1	R-UA-1/2	R-UA-1/3
Alkali resistance 0.1 M NaOH	24 h No change on the film surface (slight yellowing in solution)	1.5 h The film surface began to be affected	1 h The film surface began to be affected
	72 h No change on the film surface (slight yellowing in solution)	6 h The film completely separated from the substrate	3 h The film completely separated from the substrate
Alkali resistance 3% NaOH	24 h The film surface began to be affected	-	-
	72 h The film completely separated from the substrate	-	-
Acid resistance 3% H_2SO_4	72 h No change	72 h No change	72 h No change
Salt resistance 5% NaCl	72 h No change	72 h No change	72 h No change
Water resistance Distilled water	18 + 2 h No change	18 + 2 h No change	18 + 2 h No change
Solvent resistance methanol, toluene, ethyl acetate, acetone	30 min No change	30 min No change	30 min No change
Environmental resistance wet-dry-heat cycle	10 cycles No change	10 cycles No change	10 cycles No change

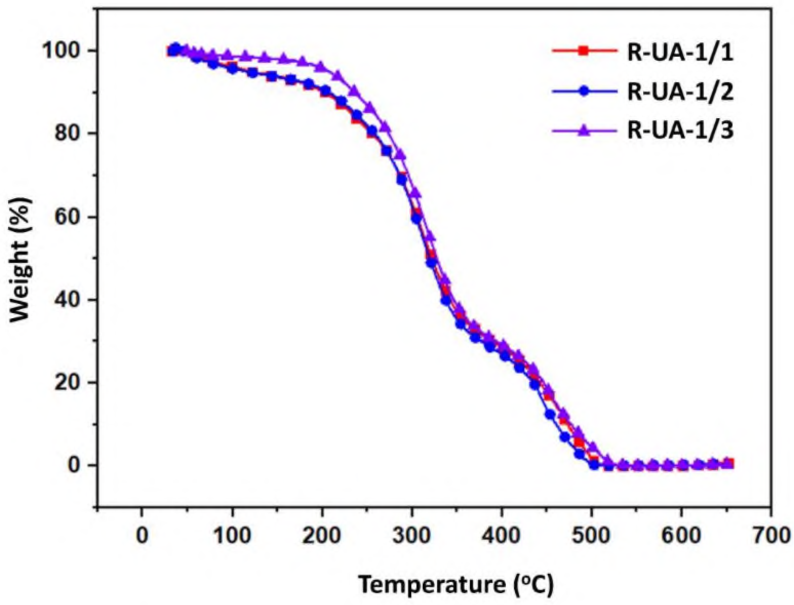

Figure 2. TGA curves of urethane-modified alkyd resin films.

3.4. Urethane-Modified Alkyd Resin Based Paint Production

To prepare the B-1/1 paint, a process was carried out in two stages using the urethane-modified alkyd resin (R-UA-1/1) with an NCO/OH:1/1 as a binder. The pigment paste was combined with other paint components and additives to create a stable dispersion system. The composition of the pigment paste (PP-1/1), and the formulation of the solvent-based urethane-modified alkyd paint (B-1/1), prepared with R-UA-1/1 resin diluted to 65% solids with xylene, are presented in Table 3 and Table 4, respectively.

Table 3. The composition of the pigment paste (PP-1/1).

Component	Ratio (wt.%)
Binder, R-UA-1/1 resin (65% in xylene)	71.29
White pigment/filler, TiO_2	14.26
Colored pigment (Bayer, iron oxide yellow)	14.26
Additive, bentone (rheological agent, anti-slump and anti-slip additive)	0.18
Dispersion and wetting agent (DISPERBYK-108)	0.02

Table 4. The formulation of the solvent-based urethane-modified alkyd paint (B-1/1).

Component	Ratio (wt.%)
Pigment paste (PP-1/1)	18.68
Binder, R-UA-1/1 resin (65% in xylene)	78.60
Additive, butyl alcohol (brushability and flow improving agent)	1.87
Additive, soy lecithin (wetting and dispersing agent additive)	0.40
Additive, bentone (rheological agent, anti-slump and anti-slip additive)	0.23
Dispersion and wetting agent (DISPERBYK-108)	0.23

The preparation of B-1/1 paint occurred in two stages. In the first stage, a pigment paste (PP-1/1) was prepared. For this, the components listed in Table 3 were loaded into the mixing chamber of the high-speed laboratory-type disperser. This composition was mixed at a peripheral speed of 12-14 m/s, and homogenization was achieved. In the second stage, the other paint components and additives in Table 4 were added to the prepared PP-1/1 pigment paste. The mixing speed was gradually increased, and finally, the system was continuously mixed at a peripheral speed of 20 m/s, which was sufficient for complete dispersion. At the end of this process, which lasted for a total of 70 min, a urethane-modified alkyd resin-based paint system (B-1/1) was successfully prepared. After preparation of the paint, it was diluted to 75% solids content using xylene.

3.5. Wet Paint and Dry Paint Properties of Urethane-Modified Alkyd Resin Based Paint

The properties of urethane-modified alkyd resin-based paint were determined by "wet paint tests", "dry paint tests (physical coating tests)", and "household chemical resistance tests (chemical coating tests)".

3.5.1. Wet paint properties

Wet paint test results applied to B-1/1 paint under room conditions are presented in Table 5.

Table 5. Wet paint test results of B-1/1 paint.

Wet paint tests	Results
Solids content	75% (wt.)
Flow time (with DIN Cup, 8 mm/21^{o}C)	42 seconds
Dynamic viscosity (with Brookfield DV2T rotary viscometer)	33270 cP
Density (with BYK density-cup)	1.07 g/cm^3
Hiding power (with BYK Byko-chart)	0.0269 g/cm^2
Particle size (with 100µ BYK grindometer)	7.5 Hegman / 6.5 µ

As the viscosity value of paints increases, the flow time also increases. The dynamic viscosity of the prepared urethane-modified alkyd resin-based paint was found to be 33270 cP, and the flow time was 42 seconds. The density, hiding power, and particle size values of the paint are in the suitable range for paint applications [8, 22].

3.5.2. Dry paint properties

Before dry paint tests of B-1/1 paint, a mixture of driers was added to the diluted paint formulation at a ratio of 1.12% (0.28% Co + 0.14% Mn + 0.42% Zr + 0.28% Ca) by weight of the total formulation [22] and mixed in the disperser at 20 m/s peripheral speed for 10 min. Then, 100 µ paint films were prepared with the BYK applicator.

Primarily, the drying degrees of the solvent-based paint film were determined in the air, and the results are presented in Table 6. The physical dry paint properties of the paint film oven-cured at 110^{o}C for 2 h are presented in Table 7. In addition, the solvent and environmental resistance test results are also presented in Table 8.

Table 6. Drying degree test results of B-1/1 paint in the air.

Time	Drying degree
1.5 h	Dry to touch
3 h	1st stage
4 h	2nd stage
7 h	3rd stage
24 h	4th stage
48 h	5th stage
72 h	5th stage

At the end of the drying time test applied to the 100 µ paint film, it was observed that the paint film reached the 4th stage after 24 h, and the 5th stage after 72 h. The paint film, which reached the dry-to-touch stage in 1.5 h in the air under room conditions, achieved the highest drying degree (7th stage) after 2 h of oven-cured at 110^{o}C after remaining in these conditions for 72 h. All other physical and chemical surface coating tests were applied to oven-cured films.

Table 7. Physical dry paint test results of B-1/1 paint.

Dry Paint Tests	Results
Drying degree (Modified Bandow Wolf test method)	7th stage
Abrasion resistance (Falling sand test method)	18000 mL sand
Adhesion strength (Cross-cut test method)	%100
Impact resistance (Falling weight test method)	50 kg x cm
Pendulum hardness (König Pendulum method)	66 König seconds
Gloss (specular reflection at 60^{o} angle)	84 GU

When Table 7 is examined, it is seen that a film with excellent adhesion and high abrasion resistance was obtained from urethane-modified alkyd resin-based synthetic paint. The pendulum hardness of the B-1/1 paint was found to be 66 König seconds. For the König pendulum, the period of oscillation (damping time) of the standard glass plate is 250 König seconds [23]. This indicates that the paint film was relatively soft. Impact resistance was also slightly lower in proportion to hardness. In the standards, 70-85 GU values in gloss measurements at 60^{o} correspond to gloss coatings (6th gloss level) [24]. Accordingly, a glossy film with a value of 84 GU was obtained from B-1/1 paint.

Table 8. Solvent and environmental resistance test results of B-1/1 paint.

Solvent resistance	Time	Results
Acetone	30 min.	No change
Ethyl Acetate	30 min.	Slight swelling on the film surface
Methanol	30 min.	Slight swelling on the film surface
Toluene	30 min.	Swelling on the film surface
Environmental resistance	10 cycle	No change

As seen in Table 8, when toluene, an aromatic and non-polar solvent known as an effective solvent due to the reactivity of its methyl group, was applied, swelling occurred on the film surface. In contrast, when ethyl acetate, a moderately polar aliphatic solvent, and methanol, an aliphatic and polar solvent having a methyl group, were used, only slight swelling was noted on the film surface. Whereas, the paint film showed no signs of damage when exposed to acetone, which is also an aliphatic and polar solvent.
In the environmental resistance test (Table 8), which was performed as an accelerated simulation of periodical/circular ambient conditions in nature, it was observed that the paint film was not affected in any way after 10 cycles (1 cycle: 18 h in distilled water at room temperature + 3 h in the refrigerator at -16^{o}C + 3 h in the oven at 50^{o}C). The paint film has excellent environmental resistance.

Within the scope of household chemical resistance tests, the alkali resistance (0.1 M NaOH and 3% NaOH) test results applied by the immersion method are presented in Table 9. The results of the resistance tests against to acid (3% H_2SO_4), hot distilled water (80^{o}C), cold distilled water (room conditions, 25^{o}C), soap, and detergent applied by the immersion method are also presented in Table 10.

Table 9. Alkali resistance test results of B-1/1 paint.

Time	Dilute alkali solution 0.1 M NaOH	Concentrated alkali solution 3% NaOH
1 h	No change	Surface roughness
3 h	No change	Slight wrinkle
4 h	No change	Partial separation from the substrate
6 h	Surface roughness	Partial separation from the substrate
24 h	Partial separation from the substrate	Complete separation from the substrate
48 h	Complete separation from the substrate	-

As seen in Table 9, the B-1/1 paint film started to be affected by the dilute alkali solution after 6 h, and the film was completely removed from the substrate after 48 h. In the concentrated alkali solution, the film began to be affected by the alkali after 1 h. After 4 h, the film was partially separated from the substrate, and after 24 h, the film was completely dissolved and separated from the substrate.

Urethane-modified alkyd resin-based paint films showed sensitivity to alkali solution due to the hydrolysable ester bonds in their structure [15]. However, the ability of the paint film to withstand dilute alkali solution for 48 h and concentrated alkali solution for 24 h shows that this property is relatively acceptable according to the literature, and it can be improved.

Table 10. The acid, hot-cold distilled water, soap, and detergent resistance tests results of B-1/1 paint.

Test	Time	Results
Acid resistance (3% H_2SO_4)	72 h	No change
Cold distilled water (25°C)	72 h	No change
Hot distilled water (80°C)	48 h	No change
	72 h	Surface roughness
Soap resistance (8 g/L soft soap solution)	72 h	No change
Detergent resistance (1 g/L dishwashing detergent solution)	72 h	No change

In the acid resistance test presented in Table 10, which was performed by the immersion method, no effect was observed on the film surface after 72 h. The paint film, which was not affected by cold distilled water for 72 h, withstands for 48 h in hot distilled water. However, at the end of 72 h, small bubbles formed on the surface without compromising the integrity of the film. In soap and detergent resistance tests, there was no effect on the film at the end of 72 h.

Within the scope of household chemical resistance tests, the results of the alcohol, vinegar, and beverage resistance tests, which were applied spot-on and were performed using ethyl alcohol (50%, v/v), acetic acid (3% (wt.), tea (1 tea bag brewed for 5 min/100 mL distilled water), coffee (2.5 g coffee/100 mL distilled water), and cola drink, are presented in Table 11.

Table 11. The beverage, vinegar, and ethyl alcohol resistance tests results of B-1/1 paint.

Time	Beverages			Acetic acid	Ethyl alcohol
	Tea	Coffee	Cola		
1 h	No change	No change	No change	No change	No change
2 h	No change	No change	No change	No change	No change
3 h	No change	No change	No change	No change	No change
4 h	No change	No change	No change	No change	No change

When Table 11 is examined, no change/deterioration/effect was observed in the paint film after 4 h in contact with beverages such as tea, coffee, cola, vinegar (acetic acid), and ethyl alcohol. It is seen that the paint film was resistant to household chemicals.

4. CONCLUSIONS

In this study, high-performance films with hard, glossy, superior adhesion strength, high chemical, and excellent environmental resistance with good thermal properties were obtained from modified alkyd resins prepared by modification reactions of the synthesized four-component tall oil fatty acid-based and 50% oil alkyd resin with TDI at different NCO/OH (1/1, 1/2 and 1/3) molar ratios. Moreover, as the NCO/OH ratio increased, hardness, abrasion, and impact resistance values increased. At the end of all coating tests and thermogravimetric analyses, the best coating properties were observed in the R-UA-1/1 resin with an NCO/OH ratio of 1/1 among the urethane-modified alkyd resins with different NCO/OH molar ratios. R-UA-1/1 urethane-modified alkyd resin having the optimum ratio was used as a binder in the solvent-based paint formulation, and a stable paint-dispersion system without any phase separation was successfully created by combining other paint components and additives. Wet paint and dry paint tests of the prepared B-1/1 paint were performed, and it was observed that the wet paint properties were suitable for paint production. Further, paint films with high abrasion resistance, superior adhesion strength, excellent environmental resistance, glossy, and high resistance to acid, water, and household chemicals were obtained from B-1/1 paint. Considering that the paint industry needs coatings with very different properties for various purposes, even the improvable preliminary results obtained in this study are an achievement in themselves.

As a result, the production of paint with high coating performance and durability was successfully achieved by using the synthesized urethane-modified alkyd resin as a binder component in solvent-based paint production. This paint can be used as an alternative to durable coatings and alkyd paint systems suitable for interior applications.

5. FUTURE PERSPECTIVES

Our future study aims to produce sustainable, economical, and environmentally friendly waste-based paints that can compete with alkyd and modified alkyd-based paints by using the results obtained in this study and the approach of recycling and re-evaluation of waste PET.

Declaration of Ethical Standards

The authors declare that they comply with all ethical standards.

Credit Authorship Contribution Statement

The authors have contributed equally to this work.

Ferda CİVAN ÇAVUŞOĞLU: Investigation, formal analysis (all experiments, tests and analyses), validation, visualization, data curation, writing - original draft, writing - review & editing.

Işıl ACAR: Conceptualization, methodology, investigation, supervision, resources, formal analysis (support), validation, visualization, data curation, writing - original draft, writing - review & editing.

Declaration of Competing Interest

The authors declare that there is no conflict of interest.

Funding / Acknowledgements

The authors declare that no funds or grants were received during the preparation of this manuscript.

This study includes a part of the PhD thesis titled "Production of Urethane Modified Alkyd Resin from Waste PET Intermediates" prepared at Istanbul University-Cerrahpaşa in 2019.

Data Availability

All data regarding the study are presented in this article.

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