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Preparation and evaluation of linseed oil based alkyd paints

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ABSTRACT

Alkyd resins are produced with reaction of oil or fatty oil, polyol and polyacid. Alkyd resins are commonly used in coating and paint industry due to ease of application in changing environmental conditions. Linseed oil based paints executed all requirements of technical properties, drying time, storage properties, simplicity in maintenance, appearance, economy, etc. In this study, linseed oil based alkyd resins having different oil contents were synthesized

Paint formulations were prepared by mixing alkyd resin and various additives such as huntite, Aerosil R972, talc, titanium dioxide, dryer, wetting agent and anti-skinning agent. All formulations were applied on paper test plates and were dried at 30 °C. The obtained coatings were characterized by pencil hardness test, pendulum hardness test, chemical resistance test, cross-cut test, contact angle and gloss measurement. Also thermal and morphological properties were investigated by thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM) respectively. The thermal stability of the paint materials are improved with by increasing the amount of huntite and Aerosil R972 in the paint compositions.

1. Introduction

The utilization of fossil fuels for the manufacture of plastics accounts for about 7% of the worldwide use of oil and gas, which will arguably be depleted within the next 100 years [1]. The peak in global oil production is estimated to occur within the next few decades. In this age of increasing oil prices, global warming, and other environmental concerns (i.e. waste), a change from fossil feed stocks to renewable resources is important for sustainable development into the future [2]. The utilization of renewable resources can consistently provide raw materials for everyday products, effectively avoiding further contribution to greenhouse effects, because of the minimization of CO_2 emissions [3]. Therefore, academic and industrial researchers are devoted to increase attention and put on their efforts to the possible utilization of renewable resources as raw materials for the production of both chemicals and polymeric materials. The most widely used renewable raw materials are; polysaccharides (mainly cellulose and starch), proteins, sugar, natural rubber, and plant oils [4,5]. Vegetable oils and modified vegetable oils have become attractive sustainable alternatives to petroleum-based materials for industrial applications such as soaps, lubricants, coatings, paints, and, more recently, bio-plastics and composites due to their biodegradability, low toxicity, non-content of volatile organic chemicals, easy availability, and relatively low price [6]. In the past few years, consumers and individual interests in environmentally friendly paints and coating have been growing tremendously [7].

Common household oil paint, the oldest form of modern paints, uses a binder that is derived from vegetable oils, which is obtained from linseed or soya bean. Alkyd paints are based on alkyd resins (vegetable-derived drying oils), which contain a variety of polyunsaturated fatty-acid chains, commonly linoleic and linoleic acid and their triglycerides [8], which undergo free-radical-mediated autoxidation during the curing/drying process [9,10]

Alkyd resins are branched polyesters that are obtained by reacting dicarboxylic acids or anhydrides and polyols such as glycerol or pentaerythritol, and long-chain unsaturated monocarboxylic fatty acids derived from natural oils (e.g., linseed oil, soybean oil or dehydrated castor oil) [11].

Alkyd resins are susceptible to oxidative processes in the presence of catalytic systems such as light, heat, enzymes, metals, metallo proteins, and micro-organisms. Alkyd resins may undergo autoxidation, photo-oxidation, thermal oxidation, and enzymatic oxidation under different conditions, most of which involve some type of free radical or oxygen species. Then chemical drying (also called oxidative drying) occurs, a lipid autoxidation process, which means that the paint dries by oxidation of the binder compound with molecular oxygen from the air. The curing of alkyd resin is the result of autoxidation, the addition of oxygen to an organic compound and the subsequent crosslinking. This process begins with an oxygen molecule (O_2) in the air inserting into carbon—hydrogen (C—H) bonds adjacent to one of the double bonds within the unsaturated fatty acid. The resulting hydroperoxides are susceptible to crosslinking reactions. Bonds form between neighboring fatty acid

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chains, resulting in a polymer network, often visible by formation of a skin-like film on samples. [12].

Today alkyds are known as the most important and widely used resins in the coating field. They are outstanding in terms of their versatility of formulations and applications, low prices and durability. Alkyd resins are therefore can well be suited to the field of applications such as air-drying varnishes, architectural paints, and marine coatings typically in solvent-based formulations [13].

In some of the paint formulations, inorganic fillers are dispersed in a polymer matrix resulting in tremendous improvement in performance of the polymer. Mineral fillers are inert substances added to reduce the resin cost and/or improve its physical properties, hardness, stiffness, optical properties, flame resistance, thermal properties and impact strength [14]. Commonly used mineral fillers are calcium carbonate, hydrated alumina, clay, fly ash/mica hybrid and huntite [15].

Huntite ($Mg_3Ca(CO_3)_4$) is categorized in the group of salt-type carbonate minerals. The commercially used reserves of huntite are located in Greece and Turkey [16]. The attractive properties of huntite minerals are from noncorrosive to processing equipment, low smoke generation, no acid gas emission, halogen free, environmentally safe, recyclable, no combustion gas corrosion, no limitation in coloring and low combustion [17]. Also, huntite is one of the most important flame retardant additives, when it is used together with hydro-magnesite. [18] This type of flame retardant materials has been in the market since the late 1980s [19]. There have been many studies done on using huntite as flame retardant filler [20].

In this study, we investigated the utilization of linseed oil in order to obtain alkyd resin, by changing the oil content. It was synthesized from medium oil resins (48%) and long oil resins (60%). In the first step of the resin synthesis, alcoholysis, linseed oil and trimethylolpropane were reacted using calcium carbonate as a catalyst. In the next step, polyesterification, the monoglyceride was reacted with phthalic anhydride. The reaction was controled by the acid number (AN), which should be under 15 mg KOH/g of resin in the end of the reaction. The obtained resins were characterized by ATR-FTIR and ^{1}H NMR techniques. Then, linseed-based alkyd resins were used in paint formulations. In addition, huntite, Aerosil R972, talc, titanium dioxide, dryer, wetting agent and anti-skinning agent were used in the paint formulations. The paint materials were characterized with the analysis of various properties such as hardness, gloss, cross-cut adhesion, chemical resistance test, contact angle measurement. Thermal and morphological characteristics of the paint materials were determined by using thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Materials

Linseed oils were supplied by Arifoğlu Chemical. Trimethylolpropane was provided by Sigma Aldrich. Calcium carbonate ($CaCO_3$) was recieved from Merck. Phthalic anhydride, talc, Titanium dioxide (TiO_2), Cobalt(II) naphthenate, Zirconium naphthenate and Calcium naphthenate (drying agents), Antiterra 204 (wetting agent), methyl ethyl ketoxime (MEKO) and anti-skinning agent were supplied from Kayalar Chemical A.Ş. SiO_2 (Aerosil R972) was purchased from Evonik Industries and used as received. Huntite ($Mg_3Ca(CO_3)_4$) was obtained from Denizli, Turkey. Common solvents such as methanol, xylene, toluene, ısopropyl alcohol, dietylether, hexane and methyl ethyl ketone (MEK) were used as received.

Table 1
Formulation of different linseed oil based alkyd resins.

	AKD 1 (48% oil content)	AKD 2 (60% oil content)
Linseed oils (g)	50	80
Phthalic anhydride (g)	30.11	30.11
Trimethylolpropane (g)	23.16	23.16
Calcium carbonate (g)	0.4	0.64
Xylene (g)	10.82	13.32

2.2. Characterization

FT-IR spectrum was measured on Perkin–Elmer Spectrum100 ATR-FTIR spectrophotometer. ^{1}H NMR spectrum was recorded by using a Varian model T-60 NMR spectrometer operated at 500 MHz. Other coating properties were also measured in accordance with the corresponding standard test methods as indicated. Cross cut (DIN 53151), pencil hardness (ASTM D-3363), pendulum hardness (DIN 53157), and gloss (ASTM D-523-80) were performed to determine the physical properties of the coatings. MEK rub test (ASTM D-5402) was performed to check for the thorough curing of the coatings; the surface was inspected for visual changes in appearance. The wettability characteristics of free films were performed on a Kruss (Easy Drop DSA-2) tensiometer. The contact angles (θ) were measured by means of sessile drop test method in which drops were created by using a syringe. Measurements were made using 3–5 μl drops of distilled water.

The viscosity of the paint formulations were measured by using a Krebs Unit Viscometer Model KU-2 viscometer. The measurements were done under atmospheric pressure and at 23 °C temperature. Thermogravimetric analyses (TGA) were performed using a Perkin–Elmer Thermogravimetric analyzer Pyris 1 TGA model. Samples were heated from 30 to 750 °C with heating rate of 10 °C/min under air atmosphere. SEM imaging of the films were performed on Philips XL30 ESEM-FEG/EDAX. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating.

2.3. Synthesis of linseed oil based alkyd resin

Linseed oil based alkyd resin was synthesized in two stages. Linseed oil was charged into three-necked round bottom flask equipped with a thermometer, mechanical stirrer, condenser, Dean-Stark trap and a nitrogen inlet. The oil was heated to 200 °C. The formulations of alkyd resins having different quantities of oil content are given in Table 1. The trimethylolpropane as a reactant and calcium carbonate (catalyst, oil 0.8% up) were added. After the addition linseed oil was heated to 240 °C. Small samples were taken and diluted in anhydrous methanol. If the resulting solution

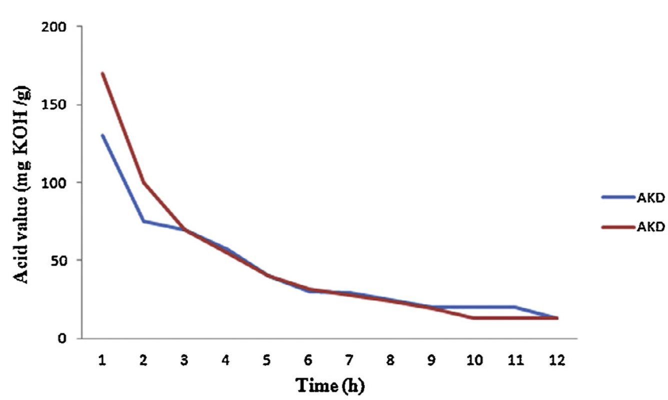

Fig. 1. The acid number versus the reaction time for different alkyd resins.