Effects of composition variations and curing conditions on the gloss of water reducible clear coatings prepared from palm stearin alkyds

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Introduction

Alkyds are tough resinous materials formed by reacting polybasic organic acids (polyacids) with polyhydric alcohols (polyols). Broadly speaking, the reaction produces resins of the general class of polyester. The notable difference between an alkyd and other polyesters is the presence of monofunctional fatty acids from vegetable oils as a major part of its composition.

Alkyds have been a part of the coating industry since 1926 and they have enjoyed a consistent annual growth. Due to their versatility and performance on metal substrates alkyds have become an important class of synthetic resins, accounting for more than 50% of all those used by the paint industry. Properties associated with alkyd-based coatings include fast dryness, good corrosion protection, high gloss and the ease of application even over poorly treated surfaces. The alkyd reaction is accepted as being the most versatile resin-forming reaction known. No other resin lends itself to greater internal variation or to more useful modification by physical or chemical blending with other polymers.

Traditionally, alkyds have been produced in aliphatic or aromatic solvents at low solids content so that paint formulators could use high level of low cost solvents to keep overall paint prices low. With the advent of safety considerations and of the regulations against air pollution by solvent-borne coatings and the alkyd industry has been investigating alternative raw materials and formulations. The ultimate intention is to reduce the overall content of volatile organic compounds (VOC) in an air-drying coating material and to improve the performance.

Two viable approaches for reducing the VOC are the development of high solids and water-reducible alkyds. These alkyds are markedly different from the conventional solvent-based materials, and both can contribute to low solvent demand by different formulation techniques. Conventional solvent-based alkyds have molecular weight from 40,000 to 100,000. They have relatively low levels of excess hydroxyl functionality and a higher degree of branching. On the other hand, the usual molecular weight for high-solids alkyds ranges from 12,000 to 20,000. They tend to have higher hydroxyl numbers and less branching on the polymer backbone. By contrast, water reducible alkyds must contain a sufficient acid value for neutralization with ammonium hydroxide or amine and must be miscible with water.

During the manufacturing process of alkyds, raw materials may be introduced as such or combined with some other materials. Thus, the fatty acids may be added, combined with glycerol, as an oil molecule. There are some obvious advantages in using oil rather than free fatty acids. Oil is cheaper, less corrosive and less susceptible to discoloration than free fatty acids. The oil length of an alkyd refers usually to the oil portion of an alkyd expressed as a percentage of the final alkyd weight. Currently, the main vegetable oils for high-performance, low-VOC, air-drying alkyds include soybean, linseed and castor oils.

The oil palm, Elaeis guineensis, was first introduced into Malaysia as an ornamental plant in 1870, whilst the first commercial planting took place only in 1917. Due to the encouragement of the government by various incentives, rapid development of palm oil industry took place, and by 1966 Malaysia had become the world's largest producer and exporter of palm oil. Recently, there have been continued interests in diversifying the uses of palm oil, and one of them is in the making of alkyds.

Palm oil consists of about 94% triglycerides, 4% free fatty acids and 1% of other minor constituents. The triglycerides contain about 50% saturated fatty acids, 40% mono-unsaturated fatty acids, and 10% di-unsaturated fatty acids. These fatty acids almost exclusively have an even-number of carbon atoms, the majority of which are C-16 and C-18. The principal saturated fatty acids are palmitic acid (hexadecanoic acid) and stearic acid (octadecanoic acid), whereas the unsaturated fatty acids are oleic acid (cis-9-octadecenoic acid) and linoleic acid (cis-9,12-octadecenoic acid). The fatty acid composition of palm oil is very similar to that of tallow oil which is one of the world largest source of fatty acids. In principle, hydrogenating palm oil can produce the entire range of fatty acids found in tallow oil.

Palm oil is usually fractionated to separate the higher melting stearin from olein that has a clear point of around 25°C. The olein fraction is a very suitable frying medium and an excellent table and cooking oil. The cheaper stearin fraction can be used by oleochemical industries for the production of palmitic and stearic acids, soap and food emulsifiers.

Recently, a series of water-reducible alkyds was prepared from palm stearin. These alkyds, with oil length 28, 33 and 45, with a similar average molecular weight of around 1100 and acid values around 50, have shown good film forming properties as clear stoving materials prepared by mixing 4 parts of alkyd resin with 1 part of a methylated melamine resin. Differential Scanning Calorimeter (DSC) measurements have been used to study the curing in the temperature range of 110–155°C. Alkyds of shorter oil length were found to produce harder films that were, however, more brittle. The gloss of these enamel coatings were not very good. Further investigations have shown that the gloss of such coatings could be improved substantially by adjusting the formulation and the curing conditions.
paper presents the results of the effects of varying these factors on the gloss of the coating.

**Experimental**

**Instrumentation**

Thermogravimetric analysis (TGA) of each clear coating material was performed using a Rheometric Scientific TGA instrument (Model 1000+). A Sheen trimicrogloss meter was used for measuring the gloss of the coatings.

**Materials**

The palm stearin was donated by the Pasir Gudang Edible Oil Pte Ltd. Other chemicals, as listed below, were commercial grades and were purchased and used without further purification. Phthalic anhydride was from P.T. Petrohidada, Indonesia, glycerin (99.5% PH. EUR) from Henkel Oleochemicals (M) Pte Ltd., phosphoric acid from Albright Wilson (M) Pte. Ltd., n-butanol from Mobil (M) Pte. Ltd., butyl cellosolve from Dow Chemical, USA, mono pentaerythritol, phthalic anhydride and benzoic acid from Perstorp AB, Sweden, trimellitic anhydride from Amoco Corporation, USA, benzoic acid from Velsicol Chemical Corporation, USA, lithium hydroxide from FMC Corporation, USA, AMP-95 (2-amino-2-methyl-1-propanol, 95% in water) from Angus Chemical USA, and the methylated melamine formaldehyde resin, Cymel 303, was from Cytec USA.

**Methods**

Preparation of water reducible alkyd resin

Three water reducible alkyds designated as WRA28, WRA33 and WRA45 having oil length of 28, 33 and 45 respectively were prepared. The calculated amounts of palm stearin and mono pentaerythritol were mixed in a round bottom flask fitted with a Dean and Stark tube and a stirrer. 1.2 g lithium hydroxide was added and the mixture heated to 230°C and held until alcoholysis was complete. The mixture was allowed to cool down to 200°C and 1.2 g of phosphoric acid was added, followed by the requisite amounts of mono pentaerythritol, phthalic anhydride and benzoic acid. Xylene was added in small amounts to maintain reflux at 210°C–220°C and the water generated was collected at the decanter arm. The reflux mixture was sampled periodically to check the acid value. The calculated amount of trimellitic anhydride was added when the acid value fell to 20. Reflux was continued at 175°C until the final acid value reached approximately 50. The mixture was allowed to cool to 120°C, and a 1:1 mixture of n-butanol and butyl cellosolve was added. The resin was rendered water-reducible by the addition of AMP-95 as part of the thinner (1 part butyl cellosolve to 3 parts water).

**Formulation of clear coatings with different alkyd/melamine ratios**

The solid content of each of the water-reducible stearin alkyd was determined by drying a small sample in an aluminium cup at 120°C to constant weight. Calculated amounts of the alkyd and Cymel 303 resin (containing 98% solid hexamethoxymethyl melamine) were mixed and diluted with dilution thinner so that the final mixture contains about 60–70% solid. Five clear coats were prepared from each of the alkyds with the following proportions of alkyd to melamine: 55/45, 60/40, 70/30, 80/20 and 90/10. No other additive was used in these formulations.

**Preparation of panels and curing conditions**

When necessary, the clear coating material was adjusted to spraying viscosity (30 second/ NK=2) with water, and applied by an Iwata spray gun (model n-71) at a pressure of 40–45 N/m² on a phosphated mild steel panel (7cm × 20cm). Four passes were necessary to obtain a dry film thickness of 25–50 µm as measured with a thickness meter. The sprayed panel was then flashed off for 10 minutes at room temperature before being cured in an air oven for 30 minutes. Curing at 120°C, 140°C, 160°C, 180°C and 200°C was investigated.

**Thermogravimetric analysis (TGA) of clear coatings**

For each of the alkyd resins, selected clear coatings with different alkyd/melamine ratios were subjected to TGA measurements. About 6–8 mg of the sample was heated in a nitrogen atmosphere from 40°C to 800°C at a heating rate of 20°C min⁻¹. It was found that the initial sample (at 55–60% solid content) was more suitable for loading into the sample crucible at room temperature since it was viscous enough to minimise weight loss in the presence of purging nitrogen, before the heating programme started. The sample diluted for spraying contained more solvent, and the weight loss started immediately after mounting the sample in the presence of purging nitrogen even before the heating programme was activated.

**Gloss measurements of the cured panels**

Specular gloss was measured according to ASTM D523. Measurements were made at least 1 cm away from the edges. A total of 10 readings was taken: 3 spots from the top, 4 from the centre and 3 from the bottom of each panel. The average of the readings was taken to represent the gloss of the panel.

**Results and Discussion**

Characterisation of these alkyds has been described elsewhere. Measurements of Tg by Differential Scanning Calorimeter (DSC) have been used to check the state of cure of the coatings. As expected, with a mixture of products there was a range of thermal transitions when the coatings were not cured properly. Surprisingly, as the curing reactions proceeded at suitable temperatures, the DSC measurements showed well defined Tg's which increased to a maximum...