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# Alkyd resins: From down and out to alive and kicking

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ABSTRACT

Alkyd resins have been introduced in the 1930s as binders for paints. Their compatibility with many polymers and the extremely wide formulating latitude made them suitable for the production of a very broad range of coating materials. This includes do-it-yourself paints and varnishes for wood and metal, road marking paints, anticorrosive paints, nitrocellulose lacquers, two-component isocyanate curing coatings, acid curing coatings, stoving enamels, etc. Except for phthalic anhydride, being of petrochemical origin, the other raw materials used in the synthesis of the alkyds are from biologically renewable sources. This, combined with their biological degradability, makes them very interesting binders from an ecological point of view. Solvents which are used to reduce and adjust the paint viscosity are the only concern with respect to the ecological aspects of the alkyd paints. In recent years, however, we witness quite an activity in designing alkyd emulsions and high solids alkyds which can serve as binders for environmentally friendly coatings.

It can be expected that in coming years the contribution of common low(er) solids alkyds in organic solvents will decrease, those products being replaced with high solids alkyds, alkyd emulsions and other high end waterborne binders. High end in this respect means all waterbased systems that exhibit a performance substantially higher than common thermoplastic latices used for wallpaints.

When properly formulated, alkyd emulsions can be considered as candidates to formulate paints with a zero VOC level. This paper summarizes the new developments in alkyd emulsions and high solids alkyd paints and compares these paint systems with paints based on acrylic dispersions as other environmentally friendly alternatives to conventional paints.



## 1. Introduction

The environmental impact of the coating industry is mostly associated with the VOC level of the paints. Recent developments, however, indicate that the paint industry is more and more confronted with regulations that stretch beyond the VOC emission. The pollution control is not only limited to air pollution but also includes the pollution of water, marine environment, land contamination and even the pollution caused by packaging waste. The health and safety factors are taken into consideration in the legislation acts that regulate the conditions of the workplace and equipment, the occupational exposure to different chemicals and the major accident hazards. Next to this, specifically for the consumer products the consumer protection plays a very important role with repercussions to the product safety [1]

In recent years attention has been paid to the complete environmental performance of the paints using the life-cycle assessment as a technique that considers the total ecological impact of the product. The life-cycle assessments of different types of decorative paints for both the do-it-yourself and the professional market have been extensively reported in a number of papers [2–5]. The environmental pressure on the paint producers has resulted in the development of a number of water-borne products that have been brought into the market. Most of these products for the decorative sector are water-borne acrylic paints. In recent years, parallel to the water-borne acrylics, environmentally friendly products based on alkyd emulsions and high solids alkyds as binders have been commercially introduced. The analysis of the properties of these materials and the comparison with the water-borne acrylic paints show a number of advantages of the alkyd based environmentally friendly paints.

## 2. The history of alkyds, the start of an era

The first alkyd resin was synthesized in the mid-1920s by Kienle, who combined the already known technology of producing polyester resins based on glycerol and phthalic anhydride (the so-called Glyptals) with the empirical knowledge of producing oleoresinous paints already existing for several centuries. Kienle also classified the alkyd resin in three groups: long, medium and short oil resins, a classification nowadays still in use. Full-scale

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commercial production of alkyd resins began in 1933 at General Electric and it was followed by other companies after in 1935 Kienle's patent was ruled invalid because of the anticipation of prior art [6]. Shortly after commercialization started, the alkyd resins enjoyed explosive growth replacing the oils as binders in the old-fashioned oleoresinous paints offering much better coating properties at a very attractive price.

Distinguished feature of the alkyd resins is the possibility of using the same chemistry to develop a number of products with very different properties. By changing the oil length and suitable modifications with chain stopping agents, phenolic resins, acrylic monomers, styrene, vinyl toluene, silicones, isocyanates etc., one can design alkyd resins suitable for a broad range of applications. Another important characteristic of the alkyd resins is their compatibility with a number of polymers such as nitrocellulose, phenolic resins, epoxy resins, amino resins, silicone resins, chlorinated rubber, cyclized rubber, hydrocarbon resins, and acrylic resins. This makes them very versatile polymers to produce a broad range of coating materials such as do-it-yourself paints and varnishes, transparent and semi-transparent stains, road marking paints, anticorrosive paints for metal protection, nitrocellulose lacquers and paints, two component isocyanate curing coatings, acid curing coatings, and stoving enamels for general metal application and coil coatings. There is hardly any other group of binders with a comparable formulating latitude like the alkyd resins.

The commercial success of the alkyd resins was backed up by extensive theoretical work on non-linear polymerization [7–10] followed by numerous methods for calculating the formulations of the alkyd resins [11–23].

It could be said that specifically after the Second World War, the research on solvent-borne alkyd resins took the quality of these binders to a level that approaches the maximum that can be achieved from technical point of view.

The development of new polymers and resins for the paint industry resulted in the introduction of new binders that have considerably damaged the position of the alkyd resins. Traditional thermoplastic latices have taken a considerable part of the decorative market, the polyester resins for liquid and powder coatings dominate nowadays the general industrial market and the coil coating market, numerous types of new coatings like two component acrylic or polyester isocyanate coatings, polymer dispersion based coatings and radiation curing coatings have to a large extent pushed aside the alkyd resins from the industrial wood market.

Due to the environmental pressure and the competition by the traditional thermoplastic latices that appeared in the market in the 1950s, alkyd resin producers have started with the development of an environmentally more friendly version of their products. The first concept was based on the synthesis of alkyd resins with a relatively high acid value which upon neutralization with amines can be transferred to a form of colloidal solutions in a blend of water and water miscible solvents of glycol ether types. In the 1970s in the laboratories of Amoco Chemicals Company a number of water soluble alkyd resins were developed with a rather broad application range [24,25]. Although the resins produced according to this principle offer environmentally better alternatives to conventional alkyd paints, the total ecological burden is not significantly lower. The solvent content of 20–30% and the presence of amine considerably distort the ecological image of these coatings. Next to this, the alkyd paints based on these binders suffered from a number of disadvantages. The presence of amine results in slow drying and through-hardening properties combined with rather poor yellowing resistance. Because of the colloidal nature of the system water reducible alkyd paints manifest a viscosity anomaly when thinned down with water causing nasty problems during the application. And finally, the high pH of the system (usually pH > 8) causes slow hydrolysis of the ester bonds, adversely affecting the storage stability. All of these factors were big obstacles to the commercial success of this system specifically in the do-it-yourself market. With minor success these water-reducible alkyd resins are still used for the production of water-borne paints for industrial or semi-industrial application.

## 3. Development of even more environmentally benign alkyds in the last decennia

### 3.1. Alkyd emulsions

In the 1980s and 1990s we witness quite an activity in designing alkyd emulsions as another version of environmentally friendly alkyds. Theoretically speaking alkyd emulsions can be considered as candidates to formulate paints with a zero VOC level, and when properly formulated with the right choice of surfactants the use of amines can be completely avoided. Evidence of these developments can be traced back in the literature at the end of the 1980s, most of them primarily the result of the work done in the research laboratories of DSM Resins. This early work can be summarized in the very important statement that cosolvent- and amine free alkyd emulsions can be made from most alkyds provided the resin viscosity is not too high and sufficient shear forces are applied in order to achieve a low particle size that ensures storage stability [26–28].

A number of publications and patents describe various approaches to improve the properties of the alkyd emulsion paints with a goal to bring them to a level equal to the one achieved by conventional alkyd paints.

An interesting method to eliminate the use of conventional surfactants is the preparation of alkyd emulsions by in situ polymerization of hydrophilic monomers within solventless alkyd resin followed by inverse phase emulsification has been reported [29].

The use of polymerizable surfactants in the preparation of alkyd emulsions has been discussed by Holmberg [30–32]. It is claimed that properties of dried film have been considerably improved by reducing the surfactant migration from the bulk to the film surface. Short oil alkyd resin emulsion has been recommended in the preparation of acid curing wood lacquers in combination with water soluble amino resins [33].

Urethane groups containing alkyd emulsions prepared by reacting low molecular weight alkyd resins with dimethylol propionic acid as a source of carboxyl groups and isophorone diisocyanate, having molecular weights between 10,000 and 70,000, have been described in a patent of Bayer [34]. Coatings obtained with these binders are characterized with good water- and solvent resistance, high hardness, elasticity and gloss.

In an attempt to solve the problem of grinding pigments in an alkyd emulsion paint, a disclosure of BASF describes a system which consists of acid functional acrylic polymer dissolved in butyl glycol and neutralized with an organic base which serves as grinding medium and at the same time as stabilizer for the alkyd resin which is emulsified by vigorous stirring in the already prepared pigment paste [35]. It is claimed that these protective coatings, which do not require hydrophilic additives (emulsifiers, protective colloids, pigment wetting agents) have a good water resistance. Commercial types of amine- and cosolvent free alkyd emulsions have been introduced in Europe in the second half of 1991 [36]. In 1993 DSM Resins started to emulsify high viscous alkyds by a new emulsification technique. In this way, it is possible to produce short oil alkyd emulsions with properties that potentially outperform those of the conventional alkyds.

Alkyd paints dominated the architectural coating market for a long period until the appearance of polymer dispersion or the so-called latex paints. Specifically for wall application water-borne paints based on polyvinyl acetate homo- and copolymers, styrene-acrylics and pure acrylic latexes almost completely took over the