

Alkyds—Past, Present and Future?

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THE CONTINUING DESIRE and the need for improved appearance and performance of coatings systems in both the industrial and consumer level markets have served as the healthy stimuli to a growing industry. As a cursory historical examination of coatings will show, the evolution of currently accepted finishes has been based on the application of an expanding technology, including new materials, better means of production so as to achieve significant economics, and the full utilization of sound and fundamental principles of organic and polymer chemistry.

In the "old days" the chemical industry had not ventured forth with the wide spectrum of products so much a part of our current interest. The coatings business used natural oils, particularly linseed and tung, for many applications. The demands for rigorous performance doomed such materials to a limited life, although some, such as outdoor housepaints, are still going strong. But where weathering and resistances to water, acids, alkali, abrasion, etc. were required some extension of the "dimension" of the coating was also required.

Before linseed oil can achieve a serviceable state, it must undergo, by natural (air oxidation) or artificial means (bodying, air blowing, etc.), a higher mol wt distribution. This increase in dimension is associated with its ability to perform mechanically and physically in its application. But the resulting system is still poor in hardness, dry rate, and chemical resistances.

The happy (for the alkyd business, that is) advent of phthalic anhydride in commercial quantities and at realistic price levels stimulated the growing resin business. The ingredients for the alkyd were now at hand: the diacid, the polyol, and the fatty acid (the latter two had been disguised all along as the natural oil). The alkyd is defined therefore as the reaction product of a dibasic acid with a polyol, to which has been added sufficient monofunctional acid or alcohol to prevent gelation during processing. Briefly, each ingredient is counted upon to perform mechanistic functions, such as:

The *diacid* contributes hardness and solubility in addition to providing the links to alternating molecules of the polyhydric alcohol.

The *polyol* contributes the reaction sites for the other acid ingredients but also can be used to perform a crosslinking role via its hydroxyl groups in interaction with amino resins, isocyanates, etc. The thermal stability characteristics conferred on the polyester by the polyol also affect to a large degree the stability of the ultimate coating system. Practical tests founded on theoretical principles have established the superior heat stability of alkyds based upon pentaerythritol-glycol, trimethylolpropane, trimethylolpropane as compared with glycerol.

The *monobasic acids* contribute a wide variety of properties enabling the alkyd resin to achieve so many facets of application: air dry (slow, fast, color retentive, etc.); baking (color retentive, chemical resistant); film former; reactive resin; plasticizer; etc.

With the multitude of materials available to the coatings chemist, it is not at all surprising that there

is such confusion as to what materials should be used. Too frequently the choice is based on prejudice and misinformation rather than sound chemical fact. Although the writer might easily suggest some good starting points for such considerations, in each instance these must be qualified by cost, availability, application, processing variables, facilities, etc.

It is obvious that a low cost coating might be prepared from soybean oil, pentaerythritol, and phthalic anhydride whereas at a given time one made from tall oil fatty acid, pentaerythritol, and phthalic might be lower, equal, or higher in cost. Certainly considerations of performance features such as dry rates, gloss and color retention, and alkali and detergent resistances would be important criteria for proper choice.

But ingredient definition and choice are only part of the story. In strictly chemical terms the stoichiometry or molecular ratios require specification. Your attention is directed to the Molecular Approach to Alkyd Structure (1) and the Alkyd Composition Graph and Its Applications (2) which provide a simple means of formulating resins. These are based on fundamental mathematical and chemical principles uncomplicated by a rigmarole of mathematical nomographs and calculations. Basically, the rationale is this: maximum mol wt results in a polyester when the diacid and diol are in an equimolar or 1:1 ratio. As the result, mechanical and chemical features are bound to be greater than where other ratios would be used. Of course, certain materials require alteration of these basic approaches: phthalic anhydride forms some cyclic esters with polyols, whereas isophthalic forms little or none; some polyols are more prone to polyether formation; the esterification rates of certain acids and diacids favor the formation of linear polymer formation resulting in the proper balance of chain termination and chain propagation; too rapid polymer formation can have disastrous effects in the processing equipment by formation of gels.

The choice of an oil or a fatty acid as the modifying agent is frequently made on economic grounds. The reader is referred to the 1959 JAOCS Short Course (3). There are advantages and disadvantages to each, but it is generally accepted that greater performance values are achieved by use of acids.

If the oil is used as the source, then it is necessary to distribute (the process is called alcoholysis) some of the fatty acid groups to the unesterified polyol prior to its reaction with the dibasic acid. Otherwise the polyol and diacid may interact preferentially to form gel particles which serve only to be the source of difficulty and dissatisfaction. Specific conditions of temp, time, catalyst-type, and concentration are called for (4).

The use of acids does permit a single stage reaction where all of the resin ingredients are charged to the kettle. Developments in our laboratory known as the High Polymer Alkyd technique (5) in which delayed addition of a portion of the fatty acid is employed, results in higher viscosity and greater mol wt at a given acid number, better dry, and greater chemical resistances than in the conventional total addition techniques. But here, too, the rules must be followed; if the reaction temp in the various

stages are too high or the time of reaction too long. The process of equilibration occurs, resulting in lower mol wt resins.

Preparative-wise little need be said of the methods used other than they may be *solvent based* where a relatively closed system is used with an azeotrope forming organic liquid to facilitate removal of the water of reaction to drive the esterification to completion or *fusion* where an inert gas is used as the means of removing the water.

One of the outstanding features of alkyd resins systems is their capability of modification with other resins. Lanson has commented on this quality at some length (6). This characteristic in the past and presently has served as the continuing basis of interest for alkyds. Whatever the explanation, be it physical or chemical modification of the alkyd resin, this ability will be the source of future need and interest for alkyds.

Statistics for this branch of industrial activity are available to show that this is no small business. Although alkyds have not continued to grow at the same rate as population, still they are maintaining a significant position. In 1959, 350 million lb of alkyd resins were produced. This must be considered in the light of other new resin developments such as latex paints, epoxies, etc. Alkyd resins fit into the coatings scheme practically everywhere.

It is obvious that achievement of a place in each of the many applications, and the continued maintenance of that position against all competition on price and performance grounds is not an easy task. This is a tough business and no quarter is given; it is on this continuing demand for performance that the versatility of the alkyd resin is called upon. By proper choice of the alkyd resin ingredients themselves and selection of the modifying resin and its

amount, an infinite series of acceptable materials are provided. As new resins are produced, the horizon is further extended.

Present interest is strong in certain areas but whether this is confirmed by specific needs requires validation. Water-soluble resins have captured the fancy of the industry, but only small segments of the market have opened for coatings due to generally higher costs and restrictive application properties. Technically, air dry water-soluble coatings are within our reach today, but again the cost is a detriment. Unless some specific need exists for a water-based vehicle as is the case with some new locations where solvent paints could create hazards, little impetus in this area is to be expected.

On the other hand, the author sees a bright future for systems which approach or are synonymous with 100% solids coatings. It is apparent that raw material costs are just about as low as industry can tolerate. It then follows that application costs must be reduced. The number of coats to achieve a given film thickness must be minimized to save labor costs, and reduce film shrinkage.

Another area of increasing value to the coatings industry and affecting alkyds is collateral resin development. Any new resin which can be used to upgrade the performance or reduce the cost (not necessarily both at the same time) has something of importance for this billion dollar industry.

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Fatty Acid Derivatives in Polyurethanes¹

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THE STUDENT of elementary organic chemistry learns that urethanes are formed by the reaction of alcohols and isocyanates. He also learns that this provides a convenient method of preparing solid derivatives of alcohols that are useful for purposes of identification by means of their characteristic mp. That is generally where his knowledge of urethanes, and his interest in them, begins and ends.

The first aliphatic isocyanate was synthesized by Wurtz in 1849, and the next year Hofmann made the first aromatic isocyanate(1). During the next 80 years, particularly between 1890 and 1920, much information concerning the preparation and properties of numerous isocyanates was developed, but it was not until the 1930's that commercial applications of these compounds began to be realized. The discovery of condensation polymers such as nylon by Carothers during the 1930's stimulated interest in all kinds of difunctional materials. During this period the diisocyanates came in for their share of attention, particularly their reaction with polyhydroxy compounds to form polyurethanes.

The earliest work on the development of technical

applications of isocyanates was apparently done in Germany where, in 1937, Otto Baeyer experimented with isocyanates as a means of producing fibers equal to or superior to nylon, which would not be covered by the Du Pont patents on nylon(2). During World War II polyurethane fibers and plastics were used extensively in Germany, and a well-integrated industry based on diisocyanates developed there. Research in the U.S. was not far behind; patents were applied for in 1939 and 1940 and granted in the early 1940's. The first commercial application in this country took place early in World War II, and isocyanates were used in the production of life rafts and "Mae West" inflatable vests(2). However, really strong interest did not develop in the U.S. until after the end of the war in Germany when a group of observers sent there by the Office of the Quartermaster General returned greatly impressed with German utilization of polyurethanes. Following that, greater industrial interest developed in the U.S. and polyurethane technology developed rapidly during the 1950's.

Isocyanates and Their Preparation

It is beyond the scope of this paper to discuss the preparation and properties of isocyanates in detail,

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