Oil Modification of Alkyd Resins for Protective Coatings*

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VEGETABLE oils possessing drying properties have been used as the prime ingredients of protective and decorative coatings for centuries. One of the earliest recorded uses is mentioned by Galen, 131-230 A.D. The use of drying oils in combination with naturally occurring resinous materials to produce varnishes is indicated about the 8th century. These natural resins of the so-called fossil type have been used for centuries in the manufacture of varnishes and are used today in many varnishes to impart hardness. However, in order to dissolve these resins in the vegetable oils it is necessary to heat them to a high temperature, thereby breaking down their chemical structure and rendering them less durable.

Varnish and oil chemists for years endeavored to build up a resinous complex in the presence of the drying oils. This effort was directed primarily towards producing a varnish with greater durability than obtained with natural resins. The first partially synthetic resin was ester gum, a reaction product of rosin (abietic acid) and glycerine. This was followed by rosin modified phenol-formaldehyde resins, alkyd resins, and the 100% phenol-formaldehyde resins.

The term Alkyd was coined by Kienle in 1927 to designate products resulting from the reaction of polyhydric alcohols and organic polybasic acids or their anhydrides. As used today, the term alkyd generally refers to modifications of these resins with oils as well as natural and other synthetic resins. This type of resin starts with the chemical ingredients and builds up the resinous structure in combination with the vegetable oil itself. In other words, chemists are building up a resin-oil complex instead of breaking down a fossil resin and merely dissolving it in the oil.

The most commonly used polybasic acids and anhydrides employed at the present writing are phthalic anhydride, maleic anhydride, and to a lesser degree fumaric, succinic, adipic, sebacic, and more recently methylene disalicylic acid. By far the most important of these is phthalic anhydride, produced very cheaply by the catalytic oxidation of naphthalene.

The polyhydric alcohols employed are glycol, diethylene glycol, glycerine, pentaerythritol, dipentaerythritol, mannitol, and sorbitol. The most widely used of the alcohols are glycerine and the pentaerythritols.

An Englishman, Watson J. Smith, in 1901 first reacted phthalic anhydride and glycerine to obtain a resinous material. This resin was a hard, brittle, sticky mass requiring acetone for solution.. .The first use of drying-oil acids for modification was introduced by Kienle, who filed a patent covering this class of alkyd resins in 1927. These drying-oil-acid modified alkyd resins exhibited many outstanding properties, such as fast drying, excellent adhesion, and superior outdoor durability, either with or without pigments. This type of alkyd resin was much superior to the varnishes in general use at that time in all of these properties. Most amazing of all was the gloss retention of air dry and baked enamels using the resin as a vehicle, particularly, when exposed out-of-doors. The use of non-drying oil modified alkyd resins as an ingredient of lacquers based on nitrocellulose increased the adhesion and durability of these lacquers and are widely used for this purpose today.

MOST of the early resins were made by heating together theoretical amounts of oil acids, glycerine, and phthalic anhydride. In general, the amounts of oil acids used were less than the quantity of phthalic anhydride, resulting in resins containing 25 to 40% of oil. These first resins were prepared in open kettles of aluminum or stainless steel over open fires, according to approved varnish-making methods. This resulted in dark colored, non-uniform resins of high acid values, requiring aromatic solvents and having definite tendencies to increase markedly in viscosity upon storage, frequently becoming solid in the containers. It was also found that the high acid value of these resins caused them to react with such basic pigments as zinc oxide and basic lead carbonate.

These difficulties encountered in the use of alkyd resins were gradually overcome. It was found that the use of small percentages of anhydrous alcohols, particularly butyl alcohol, in the solvent for these resins prevented the viscosity from increasing on ageing. Longer cooking times at lower temperatures resulted in reduced acid numbers. Finally, the use of large, enclosed kettles of 1,000 to 3,000 gallons capacity with mechanical agitation and carefully controlled heating in an inert atmosphere resulted in the alkyd resins which are in use at the present day. The ingredients are carefully loaded into these kettles, all at once or as the reaction proceeds, depending upon the type of resin being processed. The temperatures are carefully regulated and recorded. When the resin has reached the desired end point, as indicated by the acid number and viscosity, the kettle is emptied. Generally, the resin is dropped from the bottom of the kettle into the previously measured solvent, well agitated, filtered, and pumped to storage tanks. At the same time, the amount of oil acids was increased to give a "longer oil" resin, reducing the percentage of polybasic acid employed. The use of more oil acids resulted in resins which were soluble in aliphatic hydrocarbon solvents, still lower acid numbers and lower viscosities. The use of resins containing up to 75% oil is not unusual today.

The most widely used fatty acids at first were linseed oil fatty acids along with smaller amounts of china wood oil fatty acids, and some soya bean oil acids. As the alkyd resin industry developed, refinements were continually introduced, forced by competition, to produce even better finishes than had ever been obtained before. One of the first refinements was the use of distilled fatty acids. These vacuum dis-

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* Presented at 19th annual fall meeting, American Oil Chemists' Society, Nov. 7-9, 1945, in Chicago.

tilled acids gave lighter colored resins to produce paler baking varnishes and more permanent white enamels, from a color retention point of view. That demand for even "whiter" whites continued until today the use of fractionated fatty acids from such non-drying oils as cottonseed and coconut oils are widely used in the manufacture of alkyd resins for the finest white enamels. The advent of the urea and melamine resins in recent years has resulted in the white baking enamels in present day use. These baking enamels consist of mixtures of urea and melamine resins plasticized with alkyd resins made from distilled and fractionated fatty acids from non-drying oils. This is the basis for the white enamels you find on refrigerators, washing machines, kitchen cabinets, and hospital furniture today. Many white and colored baking enamels are also made from alkyd resins, modified with semi-drying oil acids. The darker colored enamels still use the drying oil modified alkyds. These finishes may be applied by the usual methods of spraying, dipping, brushing, and flocoating. You will find both the air drying and baking alkyd finishes on street cars, gasoline pumps, bicycles, porch furniture, buses, automobiles, cigarette lighters, metal signs, toys, and innumerable articles in everyday use. Here they show their ability to withstand rain, sun, high humidity, grease and oil resistance, and render their protection over longer periods of time than their predecessors.

ABOUT 10 to 12 years ago it was found that alkyd resins could be prepared by the so-called "monoglyceride or alcoholysis" process. When this method is employed, it is not necessary to use fatty acids, and there is, therefore, some saving in cost. This process consists in heating together one mol of triglyceride oil and two mols of glycerine. This heating is carried out with good agitation, generally in an inert atmosphere in the presence of an alkaline catalyst such as caustic soda, calcium hydroxide, or litharge. These materials are heated together until a few drops of the mass removed from the kettle give a clear solution in alcohol. The balance of the glycerine or other polyhydric alcohol (if required) and the phthalic anhydride are then added and the reaction carried to the end point.

The introduction of dehydrated castor oil as a replacement for china wood oil was quickly followed by the use of this oil as well as the fatty acids from the oil in the manufacture of oil modified alkyd resins and has been very widely used. Many oils which were not used to any great extent in the protective coating industry prior to the advent of alkyd resins have been used to excellent advantage in these resins. We have already mentioned such acids as distilled and fractionated soya, cottonseed and coconut fatty acids. Also widely used are the fractionated fatty acids from fish oil and tall oil, the latter a waste by-product from the paper industry. Of course, the usual oils and fatty acids used by the protective coatings industry are still used for the modification of alkyd resins. These include tung, oiticica, linseed, soya, perilla, fish, and sunflower oils.

We have confined ourselves in this discussion almost entirely to phthalic anhydride-glycerine-oil modified alkyd resins. The use of other polyhydric alcohols and polybasic acids as well as other resinous modifying agents has been purposely omitted. Undoubtedly, the increased use of pentaerythritol will develop very rapidly as it was just beginning to be used before the war but was used during the war very largely for explosives. Pentaerythritol with its four primary hydroxyl groups gives a much more rapid drying product when esterified with unsaturated fatty acids than the corresponding triglyceride. Maleic anhydride gives a more viscous resin solution than phthalic anhydride, undoubtedly due to the fact that it not only forms an ester but that it may also combine with any conjugated double bonds present in the oil by the well known diene reaction.

The saturated straight chain dibasic acids, including succinic, adipic, azelaic, and sebacic acids, when combined with glycerine to form an ester, give much more flexible and rubber-like products than phthalic anhydride-glycerine resin. In general, these esters or resins are not as sticky as the phthalic-glycerine resin, and it has been found in practice that they do not have the same adhesive properties. This group of polybasic acids may be used to impart greater flexibility. Some excellent plasticisers for nitrocellulose lacquers and many other products are based on sebacic acid-glycerine resins modified with non-drying or semi-drying fatty acids.

There are two very good reasons why the use of alkyd resins will undoubtedly be more widespread in the post-war period than they were in the pre-war era. In the first place, the capacity to produce phthalic anhydride in the United States has been increased during the war. This was necessary to take care of the great quantity of alkyd resin protective coating used by the armed forces for finishing their equipment, the production of dibutyl phthalate as a plasticiser for explosives, and the large quantities of insect repellent used by our troops in the South Pacific jungle areas. The total annual capacity for phthalic anhydride in the United States which will be available by the end of this year has been estimated to be about 190 million pounds. This is an increase of several hundred per cent over our pre-war capacity. A second reason for increased use of alkyd resins in protective coatings in the post-war period is the fact that government specifications for coatings have been widely based on these resins. The manufacturers of ordnance and radio equipment, trucks, jeeps, ships and aircraft as well as quartermaster supplies have all specified alkyd resin finishes. The Army, Navy, Marine, Maritime Commission, and many Federal agencies have specified these finishes. Manufacturers have become accustomed to the fast production schedules which can be maintained by using variously modified alkyd resins. They also feel that if this type of finish meets the exacting requirements of the various government agencies, it must be good, and they want the best. This trend is also indicated by the fact that not only automobile, but also the railroad equipment and farm implement manufacturers are today looking for alkyd resin base finishes for their products. The trend in industrial finishes is for the best, at a reasonable price, and alkyd resins appear to be the best answer to date.