Drying Oils and Acids in Alkyds

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NATURAL OILS are reasonably inexpensive, available in large quantities, easily processed, and conveniently applied. Some of these materials, particularly linseed oil, have been used for a long time in surface coatings. The question therefore arises as to why we should modify these materials. The answer comes from the consideration of performance qualities for particular applications.

In some of these areas of utility, the natural oils do not fulfill the requirements of resistance to weathering, water, alkali, abrasion, etc. As a consequence, the development of oil-modified alkyd resins has gone on at a rapid pace. In essence this modification may be viewed as simply the substitution of a hard resin, in this case usually a polyhydric alcohol-phthalate condensate (polyester) for a portion of the oil. In fact, the early days of this industry used this same approach in the development of varnishes where the hard resin was one derived from rosin and phenolic derivatives.

Not only has the objective of performance improvement been achieved, together with the expansion of total area of application, but in addition natural oils, such as soybean oil, have found use. These materials of themselves possess lesser tendency to convert *via* the usual air-drying mechanisms to insoluble, permanent, and resistant films.

The use of a polyester as the modifier of the oil immediately makes the system one which has greater "dimensionability." The high-molecular-weight polyester has, because of its potentiality for conversion to still higher molecular weight and insoluble structures, the possibility of having desirable mechanical properties; adhesion, flexibility, and chemical, physical, and mechanical resistances.

The alkyd may be defined as the reaction product of a dibasic acid with a polyol modified with a monofunctional acid. With such a generalized view-point concerning the composition, the wide latitude in the choice of ingredients is apparent. Thus, according to Table I, compositions may be based upon a variety of polyols, dibasic acids of aromatic or aliphatic nature, and acids which differ in chain length as well as upon unsaturation. The focal point of the discussion involves those fatty acid modifiers which have the possibility of drying, and we shall consider both the air drying and baking conversion of such systems.

The incorporation of a fatty acid moiety on the polyester backbone permits solubility in low-cost and conveniently-used solvents. A second purpose is to achieve adequate and necessary hardness, durability, cure, and stability in the paint film. A third function is by no means a minor one. The incorporation of fatty acid in the alkyd system allows it to be processed to minimum acid number, commensurate with the application, to a stage which is not a gel. The latter has little practical utility and presents problems in removal from plant production equipment.

In view of our compositional approach to alkyd resins, one may view the ingredients from a different aspect. Two of these materials are actually available in the naturally occurring oils, such as those derived from soybean, linseed, and safflower oils. (We must also point out the availability of oils produced synthetically by modification of natural oils, such as dehydrated castor oil.) Such compositions offer a combination of a polyol, glycerol, with a mixture of fatty acids. The reactivity (ability to cross-link through catalytic or thermal effects) is related to the degree and distribution of unsaturation present in the fatty acid chain. Thus a linseed alkyd would show a greater tendency to air-dry than a comparable soy alkyd. In some other properties however, such as a lesser change in yellowness on exposure, there would be improvement with the soy composition. We are therefore led to the observation that the coatings systems must be a compromise which has to be resolved on the basis of the ultimate application.

Just as we may use oils (details of the actual preparation will be described below), it is possible to use fatty acids derived from such oils or other sources in the preparation of the resin. Keen competition exists between these two techniques of preparation in that economic factors, cost, availability, and handling and storage properties are involved. In general, the fatty acids are obtained from the oil by saponification or a variant thereof. Fatty acids from soybean oil, linseed oil, safflower oil, and dehydrated castor oil are available together with tall oil fatty acid compositions.

The formulation of alkyd systems of varying compositions (and therefore of different application) has been detailed by Kraft *et al.* (1) in several publications. The alkyd composition figure may be looked upon as a convenient solution to such problems. An examination of this device shows that, with the proper ratio of ingredients as expressed in moles, gel-free systems having wide utility may be obtained. On the basis of these concepts Figure 1 presents a table which correlates air-dry time and hardness with compositions based on tall oil fatty acid-pentaerythritol-phthalic alkyds.

TABLE I
Common Alkyd Ingredients

Polyol	Diacid	Monoacid	
		Unsaturated	Saturated
Glycerol	Phthalic	Oleic	Benzoic
Pentaerythritol	Isophthalic	Linoleic	Toluic
Trimethylolethane	Terephthalic	Linolenic	Pelargonic
Trimethylolpropane	Succinic	Eleostearic	Lauric
Sorbitol	Maleic	Ricinoleic	Myristic
α Methyl glucoside	Azelaic		Palmitic
Dipentaerythritol	Adipic		Stearic
Tripentaerythritol	Sebacic		
Glycols	Fumaric		

Alkyd Resins from Oils

As indicated previously, the natural oils are frequently used for economic reasons. Many have observed that the use of fatty acids permits a more uniform polymer structure in the alkyd resin. However, avoiding the obvious merits of each approach, to make use of the qualities of the oil it is necessary to transesterify or alcoholyze the oil with additional polyol, usually glycerol or pentaerythritol. Free hydroxyl groups are thereby generated. These are sub-

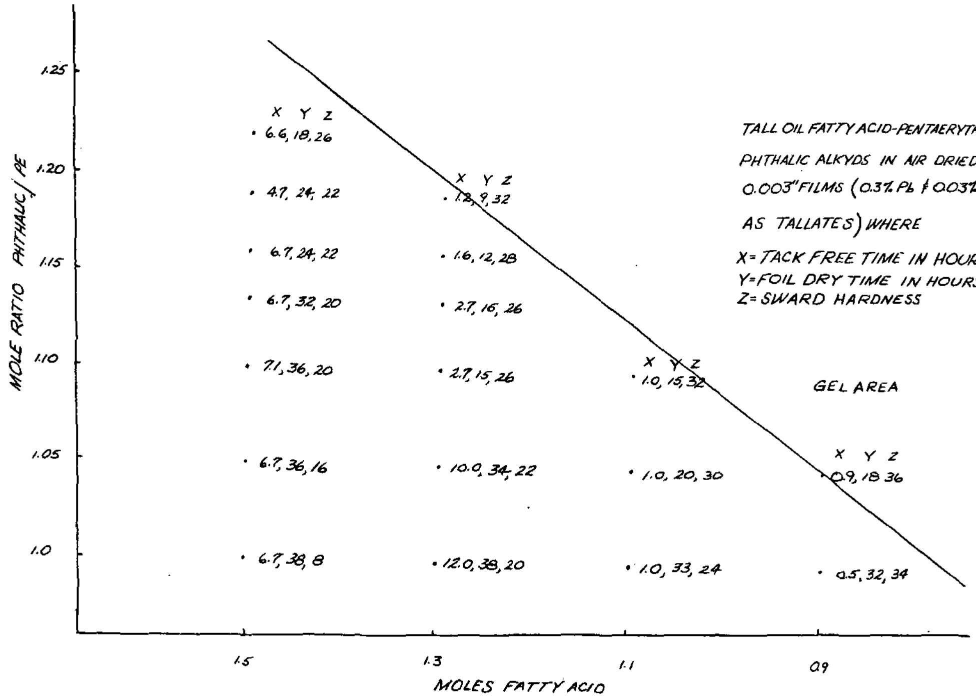

FIG. 1. Variation of film properties (dry times and hardness) with composition.

sequently reacted with a dibasic acid, such as phthalic or isophthalic, to produce the polyester chain. A recent paper by Berryman is typical of the interest in this area (2).

The alcoholysis step must be catalyzed with an acid or base since the rates of reactions without their use, even at high temperature, are too slow to be commercially feasible. Preferred catalysts, as generally used in the coatings industry, are weak and strong bases rather than the acidic types because of the poor color noted with the latter compounds. Work by Kraft and co-workers (3) indicated that low-color alkyd compositions may be achieved through proper choice of catalysts, concentration, temperature, and method of addition. Thus the best results were obtained in soybean oil, safflower oil, and dehydrated castor oil alkyds with 0.01% litherage (on oil) and in linseed oil alkyds with 0.03% lithium hydroxide. Significant improvement is noted with the proper catalyst concentration as well as the temperature for each system. A typical result is shown in Table II for soybean oil. Attention is drawn to the effects of excessive amounts of both variables on the color as well as on the clarity of the resin. Other catalysts that were evaluated presented some difficulty in view of the tendency to form difficultly-filtered alkyd solutions. These may present production problems.

The alcoholysis technique results in the redistribution of fatty acid groups from the oil to the added polyol. In order to obtain a low-color product this reaction is carried out under an inert gas blanket at temperatures in excess of 200°C. Completion of the reaction is usually detected by a solubility procedure in anhydrous methanol. The product, a "monoglyceride," is soluble in this solvent whereas the unreacted oil and possibly the polyol may not be. At best however this reaction results in a broad spectrum of compositions, as indicated by the work of Mraz *et al.* (4). It is therefore necessary that the process be largely controlled in terms of time and temperature to permit duplicability of each production batch. Inadequate reaction would result in high viscosities and tendencies toward gelation whereas extended alcoholysis may result in the loss of glycerol and possibly other polyols from the systems. Depending upon the characteristics of the fatty acid portion of the oil, temperature effects may result in increasing the viscosity of the systems to an unfavorable extent. Thus minimal time should be employed with the more reactive oils, such as linseed and dehydrated castor.

The "monoglyceride" produced by the above alcoholysis procedure is then reacted with a sufficient quantity of dibasic acid, dependent upon the ultimate composition, to produce a polymer of low acid number and particular viscosity. When this desirable situation is achieved, the product is cooled and diluted with a solvent. Filtration is frequently applied at this point in order to attain the alkyd resin solution which can serve as the vehicle for the manufacture of the final paint.

TABLE II
Effects of Litharge Catalyst Concentration and Temperature on Alkyd Resins
Soybean Oil-Pentaerythritol-Phthalic Alkyds

% Litharge on oil	Alcoholysis		70% Resin in min. sp.	
	Temp. °C.	Gardner color	Gardner color	Clarity
0.01	230	4+	5	Clear
0.01	255	5+	6	Slightly hazy
0.05	255	9+	8+	Hazy

Alkyd Resins from Fatty Acids

In the preparation of alkyd resins from fatty acids, it is common to react all ingredients at one time to the reaction temperature and process these to the appropriate acid number and viscosity called for by the particular specification. This may be done, as is possible also with the oil-modified alkyd system, by one of a number of equipment type of variations. Thus the major processing in the United States is either by a fusion process or by a solvent type. The former technique involves the elimination of the water of reaction by means of an inert gas flow whereas the solvent technique uses an azeotrope-former to achieve this end. The latter is generally preferred because of the possibilities of the greater economy of operation since less of the kettle ingredients are lost during the processing.

Techniques are available for improving resins obtained *via* these procedures. Workers at the Heyden Newport Laboratories have developed a High Polymer Alkyd Technique (5) for improvement in dry time and resistance qualities. Essentially a shorter oil alkyd is initially prepared by withholding a portion of the modifying fatty acid. The remainder of the fatty acid is subsequently added to the resin, and the entire system is reacted to low acid number. Recent work published in this Journal (6) modifies this technique to one which enables the incorporation of naturally-occurring oils to achieve improvements in film properties.

Application Areas

The final choice of a resin for a particular use depends on a number of factors including performance considerations (hardness, dry times, resistances, low color); processing requirements (ease of production, solubility in available nonirritating solvents); application properties (brushability, can stability, ease of clean-up), and economic requirements (7).

We have seen that it is possible to alter the composition of the alkyd resin by appropriate choice of the relative amounts of the "oil" and the polyester. As a result, we may within limits vary the desired film properties. Thus a long-oil alkyd, *i.e.*, one containing high percentages of oil, should offer softer films, slower drying, less resistance, and greater solubility in less powerful solvents, than a short oil alkyd where the polyester portion is in higher ratio. It is obvious that there may be several concurrent effects, some of which may be complementary, others opposing. Thus a particular hardness and dry time may be achieved with a linseed oil-modified alkyd whereas a different set of qualities is obtained with a similar soybean oil composition.

As a rough approximation, the applications may be divided on the basis of the oil-length concept. Thus outdoor house paints are presently based upon linseed oil and its polymerized version, bodied linseed oil. Here good flexibility and moderate drying speed together with some resistance to the elements are necessary. Recently however there has been some trend to the use of alkyds and "alkyd oils." These are generally long-oil alkyds, based on phthalic or isophthalic acids which will improve hardness, durability, and drying characteristics. Frequently, to avoid brittleness and loss of adhesion, some plasticizers as chlorinated wax may be added.

It is common practice to paint the trim, sash, etc., on the outside of the house with a gloss-retentive paint. Here a medium-long alkyd resin would be used. This vehicle, generally based on a soybean oil-pentaerythritol-phthalic composition, has sufficient hardness, dry time, and resistance qualities to be readily accepted by a demanding public.

On the inside of the house the full range of alkyd resins is apparent. Walls and woodwork may be painted by using long and medium oil or fatty acid resins. These may be so formulated, as in flat wall paints, to provide high viscosity and low penetration qualities to permit easy application to a variety of surfaces. Such systems must have excellent color retention in a number of atmospheres so that little color change, either by bleaching or yellowing, occurs. Resistance to high humidity conditions, strong alkaline cleaners, and abrasive cleaners is demanded in today's application. Formulation with these requirements in mind has resulted in a large number of successful paints for these uses.

The furniture in the home may be finished with vehicles that are based upon drying oils and fatty acids. In combination with other film-formers, such as urea-formaldehyde resins, phenolic-aldehyde condensates, and cellulose derivatives, these vehicles may be used in the baking type of finishes, which meet the requirements of low cost and good performance.

In the low-cost appliances a common device is to use an air-dry type of vehicle, which is baked to achieve a resistant finish. However, where the utmost in color-retentive qualities are necessary, the appliance industry has gone to the use of saturated fatty acids and oils as modifiers for the alkyd.

Other areas of application where drying oils and fatty acid-modified alkyds have found use include the automotive industry. Here such compositions are currently ingredients in metal primers and in refinishing vehicles. Again a trend toward saturated alkyds has meant greater color and gloss retention.

The Future

Where the requirement of durability is important, as in machinery, farm implements, maintenance, sport equipment, etc., it is certain that the drying oil and fatty acid-modified alkyds will maintain their position. The introduction of new competitive materials frequently raises the question as to the permanence and performance of any older materials. The alkyd however has as one of its best features the possibility of modification with other film-forming systems. Therefore we shall see a greater number of resins designed to perform specific functions by proper choice of their component parts as well as by the mechanics of their preparation.

The keen competition offered by other resin systems dispersed in water presents a challenge to the alkyd resin. The advantages of flexibility, adhesion, and durability shown by the alkyd have already won a place in combinations with vinyl polymer latices. The current development of water-based alkyds is also being watched with interest in view of the excellent performances provided in the past. The availability and acceptance of gloss and flat finishes with these systems will soon be as familiar to the consumer as the conventional solvent-based vehicles. The place of drying oils and fatty acids should therefore be maintained.

The benefits of easy modification, design for function, performance, and low cost should permit the manufacturer to achieve greater profit and the public to obtain greater value from the products of this billion-dollar business.

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Drying Oils in Printing Inks

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TWO TRENDS IN THE UNITED STATES have had a tremendous impact on the printing ink industry, mass communication and mass merchandising. There is evidence of these two trends on the newsstands and in the local supermarket every day. It is possible, with new printing equipment and paper stocks, to print a magazine in full color and to issue this magazine weekly with millions of copies. Likewise newspapers printed with some color are much more attractive and carry greater sales impact to the reader. Book-of-the-month clubs, pocket books, and other publications are constantly increasing the market for printing inks.

Mass merchandising has changed the method of purchasing for practically everyone. In today's supermarkets and department stores almost everything is prepackaged and ready for sale to the customer. Product identification is, of course, supplied by printing inks.

These two changes and the resulting increase in the volume of printing have brought about a revolution in printing speeds. To increase production, faster and faster press speeds have been used. The higher speeds have made the inks used a few years ago unsatisfactory for today's new high speed presses. New printing surfaces such as polyethylene, cellophane, polyvinyl chloride, polyesters, and others have brought up a host of new problems, such as drying and adhesion, calling for some entirely new formulations in ink. In view of these changing conditions the printing ink manufacturer finds it necessary to carry a large research program to fit tomorrow's inks to improved presses and to new papers and films.

Printing Processes

The requirements for a printing ink are based upon the method of application. There are four main methods of applying ink to the surface to be printed; they are letter-press, gravure, lithography, and flexography.

Letter-press, as the name indicates, is the pressing of a surface to be printed, usually paper upon raised letters or type. It is the oldest and by far the most important method of printing. Press sizes range from a small hand-fed press to giants that print from rolls of paper at speeds well over a thousand feet per minute and, in some cases, approaching two thousand feet per minute. Depending upon the speed of the press and the method of drying, the ink will be tailor-made for the particular press.

Gravure, or more specifically rotogravure, and again the name is self-explanatory, is a process of printing from a rotating engraved or etched cylinder. Historically gravure was first used in England for the printing of fabrics. It is now used for printing magazines and other large-volume printing. In contrast to letter-press, where the ink is carried upon a raised surface before transfer to the surface to be printed upon, rotogravure carries the ink in a recess or a cell. By varying the cell depth, gradations in the density of the color can be obtained. This gives rotogravure an advantage over other types of printing since the density can be varied from a soft highlight to a dense solid.

The graven or etched cylinder is rotated directly in the ink. The excess ink is then wiped off by a "doctor blade," which oscillates across the cylinder, wiping it clean. Since the ink is in contact with metal only and there is no rubber distribution-system involved in gravure, strong solvents such as ketones, esters, or aromatic solvents can be used in the ink formulation. Because of the simple distribution system very volatile solvents can be used, permitting rapid drying by evaporation on nonabsorbent stocks. The ability to use these strong solvents enables the ink maker to use a wide selection of film formers such as nitrocellulose, chlorinated rubber, vinyls, polystyrene, etc. Gravure drying is always by evaporation of solvent and not by oxidation.

Lithographic Method of Printing

Of the major printing processes, lithography occupies a major position both as to production and quality. Lithography differs from letter-press in essentially three ways. The printing plate used in lithography is flat (level) or very slightly etched. The printing process is accomplished in a more circuitous manner, that is, the ink is not transferred directly from the plate cylinder to stock but instead is transferred to a blanket cylinder, which in turn transfers the ink to the stock. The process is based on the principle that oil and water do not mix. In practice the printing plate is so treated that only a portion of the plate is made ink-receptive, *i.e.*, that portion of the litho-plate which does not contain the printing image is made nonreceptive to ink by the application of water to the plate. This approach has undergone further refinements in that, in some instances, ink receptivity and nonreceptivity of the plate are established through the use of specific alloys.

Flexographic Method of Printing

Flexography is another method of printing and can be called a variation of letter-press printing.