Alkyds

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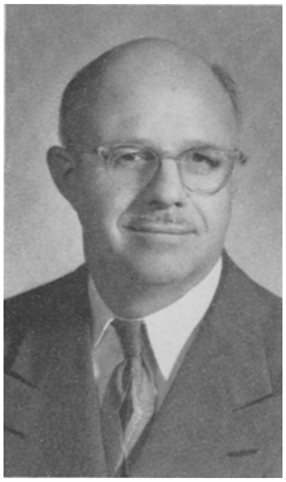
THE advent and ever increasing usage of alkyds is a tribute to the resourcefulness and foresightedness of the paint and chemical industries, and particularly to those workers in the United States who have extended their talents to bring this development to its present day status. We may fail sometimes to appreciate the strides which have been made until we reflect that as late as 1914 phthalic anhydride was a laboratory curiosity, and it was not until 1927 that the first practical alkyd was prepared. Alkyds gained their place in the paint field because they proved their superiority over oleoresinous varnishes with respect to gloss retention, quick dry, durability, and adhesion. The ever-expanding wealth of technological knowledge has given us other types of protective coatings which show improved performance over alkyds for specialized application, but basically the alkyd resin gives us the most for our money. This has been proven by customer acceptance of this type of vehicle when used either as the sole vehicle or in combination with other components. The term vehicle designates the binding and in most cases the drying portion of a pigmented formulation. Exceptions to this are in the non-drying systems. The other components mentioned previously include hardening agents, such as urea-formaldehyde, melamine, nitrocellulose, and vinyl.



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In the strict interpretation of the term an alkyd is one of the end products of the neutralization of a dibasic acid and a polyol. These can be formulated to give widely different characteristics; infusible and insoluble in some cases to the semi-fluid state in other cases. Alkyds of the latter type do have specialized uses. In general, the paint industry considers the term alkyd to designate an oil modified polyol ester of a dibasic acid, usually phthalic anhydride. Many modifications have been made, and a broad scope of usage has been developed.

The history of alkyd production dates back to 1847 when Berzelius prepared polyglycerol tartrate. Other combinations of varying degrees of importance followed in the intervening years to 1927. In that year Kienle showed that unsaturated fat acids prevented gel formation in alkyd cooks and further that the alkyd resin obtained dried on baking. This might be considered to be the starting point of the present day alkyd. The many papers by Carothers taught the fundamental concepts dealing with the formation of high polymers in general and condensation polymers (alkyds) in particular. When the basic patent U. S. 1,893,873, issued to Kienle in 1933, assigned to General Electric Company, was declared invalid in 1936, the field of alkyd manufacture became accessible to all.

Before considering the characterization of alkyds and the methods used to produce them, a review of raw materials seems to be indicated. It is quite apparent that the end use of the alkyd predicates the type of raw materials used; likewise the alkyd performance must be in harmony with the raw material price considerations. The raw materials readily available to producers of alkyds include:

A. *Dibasic Acids.* Phthalic anhydride is by far the most important with respect to usage. In varying quantities maleic anhydride, fumaric, sebacic, adipic, and succinic acids are used. From a consideration of the space configurations it follows that the first three form hard glycerol esters while the last three form softer, flexible compounds.

B. *Oils and Their Fat Acids.* In this category there are four classifications:

	Iodine Value
a) Drying	
1. Tung	170
2. Linseed	180
b) Semi-Drying	
1. Dehydrated castor	155
2. Soybean	135
3. Cottonseed	110
c) Non-Drying	
1. Coconut	9
d) Special	
1. Tall Oil	

In the recent years of fat and oil shortage, allocation of fats and oils, and more recently increased competition, tall oil has been used as a partial replacement for the oil portion of a vehicle. It is a by-product of the Kraft paper pulp industry. It is cheap, and although it has its drawbacks, it has found a place in the alkyd formulator's scheme of patterning.

The producers of vegetable and fish oils have made available to the alkyd producers a number of interesting and useful treated oils and fractionated fat acids. These vary in treatment from the incorporation of polymerization accelerants to the hydrocarbon copolymerized oils. The selected fat acids from various oils are of unusual interest in some applications. Further comment on this subject is considered unnecessary since the subject will be ably discussed by other speakers.

C. *Polyols.* Glycerine usage is predominant. However there is a trend in the business to use blends of glycerine with other polyols. These include pentaerythritol, the glycols, and multiple hydroxy compounds of the mannitol type.

D. *Solvents.* A wide variety of solvents at prices in relation to their solvency power, conveniently expressed in terms of Kauri Butanol Value, are readily available. The formulation and customer mode of application of the alkyd determine which solvent is best suited.

THE theory of alkyd resin formulation has been ably presented in detail numerous times in the past. Since the time allotted for this discussion is limited, it was considered that elaboration on this would prove time-consuming and would of necessity curtail the presentation of other material. In general, in formulating an alkyd resin, the polyol content used is in slight excess of the stoichiometric quantity required for neutralization of the carboxyl groups.

Alkyds can be classified into three groups: short, less than 40% oil; medium 40-59% oil; and long, 59-70% oil. The solubility of oil modified alkyds in solvents increases with the oil content. Formulations containing 50% or more oil are generally quite soluble in the aliphatic petroleum solvents. As the oil length is reduced, stronger solvents such as the aromatics, ketones, and low molecular weight alcohols are required.

The paint formulators have found by experience that short oil alkyds, when pigmented, have greater tendency to crack and check. As the oil length is increased, cracking and checking are not a problem, but there is a greater chalking rate at the longer oil lengths. It would naturally occur to all of you that alkyds may also be resin modified for the purposes of cheapening, hardening, speeding up the dry or controlling the rate of alkyd cooking. In general, the inclusion of resins in an alkyd formulation is deleterious to the durability.

Since the fat acid radical of an alkyd contains the points of unsaturation within an alkyd, the oil length and the type of oil used determine the initial color and color retention. It also follows that for a given oil length alkyd the through-dry and durability will vary, dependent upon the mode of drying used at the time of application. In an air dry application, drying is effected by oxidative induced polymerization of the fat acid radicals within the alkyd polymer; thus medium and some long oil length alkyds would give better through-dry, more durable films than short oil length alkyds which have been air-dried. The drying of a film during force dry, dependent upon temperature of bake, is effected largely by thermal polymerization, and it followed that through-dry and durability properties are favored by use of shorter oil length alkyds. Since alkyds exhibit rapid surface dry performance the through-dry takes considerably longer, and for this reason in force dry application the short oil length alkyd is favored. Alkyds made with low iodine number oils require some other component such as urea-formaldehyde or nitrocellulose to produce through-dry. In another criterion of performance, namely gloss retention, higher iodine oils give alkyds which show better gloss retention.

The question of driers and their effects, although important, will not be discussed in this paper.

The chemical and patent literature reveals many alkyd formulations and the manner in which they have been utilized. Factors and standards of performance for customer's approved use, which must be borne in mind when formulating an alkyd, will be listed below. It would be difficult to list them in order of their importance beyond the first one.

1. *Cost*

2. *Type of Surface to be Coated and Appearance Requirements*

Since the protective coating is the last step in merchandise production and must have eye appeal for successful sale of the whole article, it is important that the finish be right. The formulations used vary with the composition of the surface to be coated; the surface may be wood, steel, concrete, or plastic. As you all know, merchandise manufacturers' requirements vary as to gloss or sheen, others want a wrinkle finish, others want a hammerloid finish; the variations are many.

3. *Conditions of Surface to be Coated*

The pre-treatment of metal surfaces prior to finishing determines the type of formulation to be used; there must be a proper balance between adhesion and bonding on the metal surface. On wood surfaces several conditions must be determined prior to recommendation—is the wood sealed, what is the water content of the wood, is the wood treated? These and other conditions must be known.

4. *Mode of Application*

Methods of application currently used include brushing, spray, dip, and flocoat. Each type requires its own solvent balance and in some cases formulation modification. The fullness of paint film, mileage, absence of sags, and many other performance qualities are largely dependent upon the selection of vehicle.

5. *Type of Dry*

Briefly this is either of two, air dry or bake.

6. *Rate of Dry*

A wet paint or varnish film is a nuisance; the faster it dries, the better for all concerned. In the industrial field there is an ever-increasing demand for faster drying time and faster print-free time to pack. The conveyor line production type of manufacture requires that the manufacturer get his products out of the plant in a short time. If the article shows marks or imperfections due to adherence of wrappings, this requires refinishing or patching, which is time consuming, expensive, and reflects on the good will for the article. All this reverts back to the formulator: what solvent balance and what non-volatile formulation will accomplish the desired performance?

7. *Resistances*

Abrasion, humidity, heat, and cold resistances must be considered. If the finish is a floor finish, how long will it stand up under the constant treading? Will it show thermoplasticity? Another example of resistance requirements is seen in the field of furniture and cabinet finishing. The article leaving the manufacturer may be subjected to extreme cold during transporting to point of sale—should the finish cold check, you can well imagine the consternation caused.

The suppliers of paints and varnishes do a tremendous volume of resistance testing of their many formulations, current and in process of development.

8. *Color and Color Retention*

The trend towards white kitchen wall finishes and white appliances, as well as pastel colors, has been a chore for the alkyd formulators, producers, and paint formulators, as many of you well know. Even some of the deeper colors experience fugitiveness of color.

9. *Stability of Finish Prior to Use*

The alkyd formulation must be so patterned that reactivity of pigments with it will be kept at a minimum. It is obvious that if the paint is further solvent reduced because of bodying prior to use, the film so applied will give less film thickness than originally planned. This means that durabilities and appearance properties are inferior as compared to a fresher mix or to a formulation which does not require dilution.

10. *Compatability with Other Protective Coatings*

It is not uncommon for volume users of paints and varnishes to have more than one source of supply. Oftentimes the customer will use them interchangeably in his production lines or even mix them. Of necessity they must be compatible. This is just another thing for the formulator to remember.

11. *Recoatability*

For many applications the recoatability of painted or varnished surfaces is not a problem. However quite often, if the article does get additional coats of finish, it may be subjected to real abuse in mode of application or in selection of additional coatings. We must guard against such possibilities as "lifting" of the dried finish when additional finish coats are applied since this reflects back on the initial coating and its manufacturer whether the complaint is justified or not.

12. *Washability*

Now there is a tough one. Industrially, common sense with regard to washing agents usually prevails. But in the home the housewife frequently thinks of a paint or varnish as a challenge to her endurance, elbow grease, and the strongest soaps and abrasive cleaners on the market.

With all these factors, or perhaps better stated, variables, it is a credit to alkyds that their usage has attained the position it occupies. They must be good.

ALKYDS are produced by "fusion" and solvent methods. Let us first consider the "fusion" method. At one period of alkyd cooking development they were made by reacting phthalic anhydride with glycerine to a partial ester, the end point of which was characterized by the operator as a definite pill on a glass plate. At the discretion of the operator fat acid was then added and the cook allowed to proceed. As you might expect, there was always danger of gellation if the initial glycerol phthalate had been reacted too far.

The "fusion" method as currently used can be done in either of two ways: alcoholizing the oil in the presence of an alkaline catalyst at 410-430 degrees F. for about one hour followed by addition of and reaction with phthalic anhydride, temperatures ranging from 420 to 525 degrees F.; in the other procedure fat acid, polyol, and phthalic anhydride are reacted simultaneously at temperatures ranging from 420 to 525 degrees F. The latter method finds acceptance in formulations in which selected fat acids are used to effect special characteristics to the finished alkyds.

Alkyds are currently cooked in stainless steel set kettles varying in capacity from 500 to 5,000 gallons. The kettles may be direct gas-fired or jacketed to permit circulation of Dowtherm through the jacket. The set kettles are equipped with agitators and foam beaters, and provisions made for blowing inert gas through the cook as well as an inert gas blanket over the reactants.

In the solvent method a diluent such as xylol is used to effect reflux. The heating is done by the indirect fire method. The design permits the return of entrained phthalic anhydride and condensed solvent. Suitable traps permit the removal of the water of neutralization. When cooking an alkyd in which the oil is first alcoholized, it is necessary to add the diluent after alcoholysis has been effected.

In following the course of an alkyd cook, it is common practice to keep a log of not only the temperature of the reaction mass but also changes in viscosity, acid value, and cure time. The viscosity and cure time indicate the state of polymerization, thus giving the operator a guide by which to determine the end point for the cook. These determinations are easily made by competent operators who in time can correlate deviations in these logs with troubles which oftentimes can be corrected on the spot or give the supervisors and laboratory men a clue as to the causes of troubles encountered. For those unfamiliar with the term, cure time is the time in seconds required to gel a thin film spread on a thermostatically controlled hot plate at 200 degrees C. The technique requires practice before a new man can duplicate an experienced technician or plant operator. In formulations which have a fast rate of polymerization there have been cases where time did not permit the running of viscosity, the operators in those instances must and do rely on cure time data to choose the end point of the cook. The cooked batch is then dropped into reducing tanks containing the solvent, mixing them insures homogeneity.

Experience has taught alkyd formulators and producers that there is an optimum range of cure time, viscosity, and acid value for a given formulation. Divergence from these standards is to be avoided since the formulation has been designed to give the required rate of dry, durability, gloss, ease of application, and similar performance requirements.

Those of you who have witnessed and participated in the development of alkyds through the years to their present status will naturally wonder what lies ahead. How will the new raw materials affect alkyd production and usage? Already we have a preview of things to come.

Among the new materials, there is available, in small quantities, terephthalic acid. In this dibasic acid the carboxyl groups are in the para position. Its high melting point of 425 degrees C. compared to 131 degrees C. for phthalic anhydride and 52 degrees C. for maleic anhydride suggests the possibility that alkyds made with it would exhibit unusual properties.

Alkyd producers have currently been supplied with samples of sorbic acid or its derivatives. Sorbic acid is an unsaturated acid with conjugated double bonds. Its use in the solvent method of cooking should prove to be interesting in modifying and up-grading the semi-drying oils.

Tetrachlorophthalic anhydride, itaconic, 2-ethyl hexoic, and citric acids all appear to lend themselves to expanded interest and use.

In the field of polyols several new materials come to mind; polyallyl alcohol and trimethylolpropane offer interesting possibilities.

In conclusion, this paper has attempted to cover the salient points relating to alkyds and their production. It is obvious to all present that the ramifications of formulation and usage are many. The strides which have been made in this field indicate that alkyds not only have a permanent place in the paint industry but also their use will be ever expanded through the extension of studies with the new raw materials and those yet to be developed.