they presently are. However it should be noted that not too much of the work that has been done is actually fundamental in nature or takes into account the many varying sets of conditions that have been used in practice. This may be only the exception that proves the rule.

Addition and polycondensation products, such as maleic modified drying oils, have been of commercial importance. Existing products of this type have achieved a fairly important place within their field of application. While not stating that there are no problems with maleic modified drying oils, it is believed that this field has been rather thoroughly investigated and that the major problem in this general area is a study, understanding, and application of the many possible addition and condensation reactions. This is, of course an almost limitless field. A systematic study of the many organic reactions which unsaturated fatty acid esters are capable of undergoing might provide the key to many worthwhile modifications of drying oils. It might also well result, as research often does, in an unexpected bonus in the form of novel and useful oleochemicals.

IN THE BROADEST of terms the use of drying oils to prepare various oleochemicals having potential application in many fields constitutes a modification of drying oils. By way of example, unsaturated fatty alcohols have many obvious potential applications in resins, plasticizers, etc., and in the latter form might well become important factors in the coatings and related industries. Another paper already given in this symposium has pointed out how such a chemical derivative of a drying oil ("Epoxidation and Hydroxylation of Linseed Oil" by Bosch *et al.*) might make it possible to apply the drying oil in the form of an emulsion with the consequent advantages inherent in this form. In the field of oxidation lie almost limitless possibilities for the modification of drying oils, providing the oxidation can be accomplished cheaply enough. Air is a very cheap oxidizing agent, and if directed oxidation could be accomplished therewith, it seems likely that many applications would be founded on the resultant products. Finally there are several specific problems associated with one or more modified or natural drying oils which will only be mentioned. These include problems relating to drier action, yellowing and color retention, pigment-vehicle interaction in paints, odor development of coatings as they dry, etc.

The recurrent mention of cost throughout these remarks will have been noted, and it is submitted that probably the biggest unsolved problem in the modification of drying oils is economic. By this is meant that the means are already at hand to carry out many modifications of drying oils with very desirable properties for specific applications, but in general these modifications are too costly to have widespread appeal. Traditionally the processing of drying oils has been a rather low margin industry, and past experience in this area indicates that cost of any modification is a vital factor in estimating how great its application will be.

In conclusion, the modification of drying oils generally represents applied research or, in other words, the application of facts learned through more fundamental research. Where information from the latter is lacking, we are reduced to playing pool with elliptical billiard balls or a sort of research blindman's buff. Hence it is gratifying to see the stress placed on the need for fundamental information.

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IV

Unsolved Problems In the Utilization of Drying Oils In Protective Coatings[1]

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THE NUMBER and nature of unsolved problems relating to drying oils, so far as the protective coatings industry is concerned, is to a considerable extent a matter of how the term "drying oil" is defined. To a group of chemists whose professional allegiance is to processors and suppliers of naturally occurring glycerol esters, there is a host of important problems, both academic and practical, that are related to the varied uses to which these materials may be applied. To the protective coatings chemist however a drying oil problem of 1954 may no longer be a problem in 1964 or even next month if in the meantime better and cheaper finishes based upon less traditional materials are developed. Of course, there is also a good possibility that some of these less traditional, completely synthetic materials will depend upon reaction with atmospheric oxygen at sites of olefinic unsaturation for film-forming properties, and in this sense they too may be classed as drying oils. For the purposes of the present discussion I should like to ignore any problems connected with the glycerol ester nature of traditional oils and discuss only those arising from the unsaturation.

While there are many unsolved details relating to specific olefins that could be brought into this discussion, I have selected four rather general problems that will serve to illustrate the situation as it applies to the coatings industry. In view of the fact that the chemical aspects of these four problems are all interrelated, I should like to outline their practical implications first and then discuss the chemical and physical background of all of them together.

1. One of the most important properties of any drying composition is the length of time required to complete the film-formation process after application. Ideally this time should be long enough to meet the requirements of the application process but no longer. For example, in the case of a drying oil type of finish

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intended for floors, if it is estimated that the application process will require one hour, then it should be possible to walk on the floor one hour after completing the job. Similarly, if the job is expected to require one minute or one second, the finished article should be ready for use no more than an equal length of time after the last pass of brush or spray gun. Control of this order is not generally possible at present.

2. Another problem frequently encountered in the use of drying oil finishes is that of wrinkling. Most often wrinkling is something to be avoided, but certain types of finishes take advantage of this phenomenon for decorative effects. At present, control of wrinkling is an empirical art based upon trial and error adjustment of film thickness, drying time, catalyst mixture, etc. Ideally it should be possible to control wrinkling at will such that films of any desired thickness may be dried rapidly with or without wrinkling.

3. A third problem encountered in certain applications of drying oil finishes is that of yellowing. It is most often observed in white paints, such as outside house paint, that contain a high proportion of linseed or other highly unsaturated oil. The experimental facts of the color development on aging, especially in warm, dark humid places, are well known. But, like wrinkling, the phenomenon is poorly understood and is controlled empirically, often to the detriment of other properties.

4. Finally, perhaps the most important problem of all is that of durability. For many years drying oils and drying oil alkyds have been among the most durable materials available to the protective coatings industry. In recent years however new synthetic materials have been introduced that are superior in this respect, and in certain cases drying oils are being supplanted.

While research of a very high caliber, both in the United States and abroad, is being directed toward drying oil behavior, there appear to be certain aspects of the situation that have been neglected. Some of these points of neglect may be brought out by reference to the kinetic mechanism (Figure 1) due originally to Bolland (1). This scheme, or some reasonable facsimile of it, is probably familiar to everyone who has been concerned with problems of oxidation. However it is interesting to re-examine Bolland's mechanism in the light of our unsolved drying oil problems.

One important issue is the order of (R_1) with respect to metal, *i.e.*, the value of n. Woodward (2) found that the cobalt catalyzed oxidation of tetralin to be second order with respect to metal concentration. On the other hand, Bawn, working with pentene isomers, found the order to be dependent on concentration and also to vary from isomer to isomer. This is clearly important to the problem of drying oils that usually are mixtures of olefinic types and undergo large concentration changes in the course of film formation. Presently available data are by no means adequate to define the kinetic mechanisms that exist in a drying film.

Again, Bateman (3) has shown that the kinetics depend greatly upon the oxygen pressure used in an experiment as well as upon the solubility of oxygen in the olefin. In general, Bateman discovered that, with oxygen pressures over 5 mm., the termination steps R_4, R_5 could be ignored. From 1-5 mm., R_5 must be taken into account and below 1 mm., k_3, k_4, and k_5 are rate-controlling. These observations are summarized in Figure 2, which gives the reaction rates corresponding to the three distinguishable oxygen pressures under conditions where the rate of hydroperoxide decomposition can be neglected. After the steady state of autoxidation is attained, the maximum rate theory of Tobolsky (4) applies, but the equations of Figure 2 are adequate to illustrate the dependence of oxidation rate upon the oxygen pressure and the mechanism of initiation.

Bateman (3) and Bolland (5) were also able to evaluate the rate constants k_1-k_6 for a considerable number of pure olefins; these data show that the propagation reactions R_2 and R_3 and the termination step R_4 are very dependent upon olefin structure whereas the termination step R_6 is not. Also the characteristics of olefin structure that enhance reactivity of RH toward RO_2 confer enhanced stability on the derived R.'s such that the product $k_3k_4^{1/2}$ remains practically constant.

In order to apply these concepts to the process of film formation, the following considerations must be taken into account.

a) Most drying oils are mixtures of olefinic structures in which widely divergent values of k_2, k_3, and k_4 may be expected.

b) The dependence of reaction rate on metal concentration will be different for the different components and, as the solvent evaporates, the dependence of each component may change in a different way.

c) The concentration of dissolved oxygen in the film will be high at the surface and low (perhaps nil) at the substrate interface. Furthermore this gradient of oxygen concentration will be constantly shifting toward the substrate throughout the drying period so that each depth in the film will have its own characteristic sequence of changing reaction mechanisms.

d) As the film approaches complete gelation, all of the rate constants, especially of the termination steps, may be decreased by the so-called "gel effect" (6) in which free radicals are presumed to be trapped or immobilized in the cross-linked structure and their lifetimes thereby prolonged.

With these considerations in mind it is possible to examine, in an over-all sense, some of the sources of our unsolved drying oil problems and perhaps some of their cures. For example, control over the drying time rests in selection of monomer structures, catalyst types, and concentrations that will give values of k_1-k_6 that are optimum for rapid polymer formation throughout the thickness of the film over the whole drying period. This is by no means as obvious as it may sound. Thus it would be a mistake to conclude from Figure 2 that maximum values of k_1, k_2, and k_3 together with minimum values of k_4, k_5, and k_6 will lead necessarily to the shortest drying time. In the first place, it should be remembered that k_6 is not adjustable anyway and that maxima in k_3 inevitably correspond to minima in k_4. A minimum value of k_4 should lead to a maximum rate of oxidation, but the termination steps are the only ones that actually yield polymer and a reduction in k_4 might therefore be deleterious.

The gradient in oxygen concentration and hence the variation in reaction mechanisms that exist throughout the film may influence the drying time in

INITIATION	$ROOH + n\,M^{3+} \longrightarrow RO_2\cdot + n\,M^{2+} + H^+$	K_1	(R_1)
OR	$ROOH + n\,M^{2+} \longrightarrow RO\cdot + n\,M^{3+} + OH^-$		(R_1')
PROPAGATION	$RO_2\cdot + RH \longrightarrow ROOH + R\cdot$	K_2	(R_2)
	$R\cdot + O_2 \longrightarrow RO_2\cdot$	K_3	(R_3)
TERMINATION	$R\cdot + R\cdot \longrightarrow$ NON RADICALS	K_4	(R_4)
	$R\cdot + RO_2\cdot \longrightarrow$ "	K_5	(R_5)
	$RO_2\cdot + RO_2\cdot \longrightarrow$ "	K_6	(R_6)

FIG. 1

a purely physical way. Thus rapid formation of a surface skin may decrease oxygen permeability and so slow down the dry. In other words, selection of *k* values simply to give maximum attainable rate of polymer formation may not lead to the shortest drying time any more than does the maximum rate of oxidation.

Lack of time precludes any more than a brief mention of wrinkling. Burrell (7) has evolved a theory that claims the tendency to wrinkle is inversely related to the strength, or Young's modulus, of the surface skin and is independent of either the quantity or solvent power of unreacted resin beneath the skin. Consideration of the idea of a gradient in polymer concentration and composition between surface and substrate lead to a different view. Namely, the quantity and solvent power (swelling power) of the resin underneath the skin are the determining factors, providing only that the skin is at least strong enough to support a permanent wrinkle. It must also be remembered that the swelling power of the unreacted resin toward its own skin will depend upon how much chemical change the latter has undergone in formation.

Yellowing and durability should be very sensitive to variations in the relative rates of the reactions listed in Figure 1 as well as to side reactions not shown and to structural considerations not even implicit there. For example, it is obvious that the relative frequencies of the termination reactions (R_4, R_5, and R_6) will influence the proportions of RR, ROR, and ROOR structures, and hence the durability of the resulting film. Also side reactions involving decomposition of ROOH to carbonyl compounds will influence both yellowing and durability in a very complex manner. Structures of the type shown in Figure 3 have been postulated by several investigators, and qualitative identification of certain ones has been claimed. These could easily be the source of yellow color, and unquestionably all would be readily decomposed by exposure to light.

The last 10 years have seen a tremendous increase in our knowledge relating to drying oils and olefin oxidation, but, oddly enough, very little of it has been of any direct use to the protective coatings industry. As we have intimated above, one of the chief stumbling blocks to the utilization of available information is the unknown influence of the oxygen diffusion process on the reaction mechanisms. Some groundwork relating to the general theoretical problems of diffusion controlled reactions has been published (8-13), but the application of diffusion principles to the drying oil problem has not been attempted and will, admittedly, be very difficult.

$$\text{RATE } (>5\text{MM. } O_2) = R_I^{1/2} K_2 K_6^{-1/2}(RH)$$

$$\text{RATE } (1\text{-}5\text{MM. } O_2) = R_I^{1/2}/(K_2^{-1} K_6^{1/2}(RH)^{-1} + K_3^{-1} K_4^{1/2}(O_2)^{-1})$$

$$\text{RATE } (0\text{-}1\text{MM. } O_2) = R_I^{1/2} K_3 K_4^{-1/2}(O_2)$$

$$\text{WHERE } R_I = \text{RATE OF INITIATION} = K_I^{1/2}(ROOH)^{1/2}(M^{+3})^{N/2}$$

FIG. 2

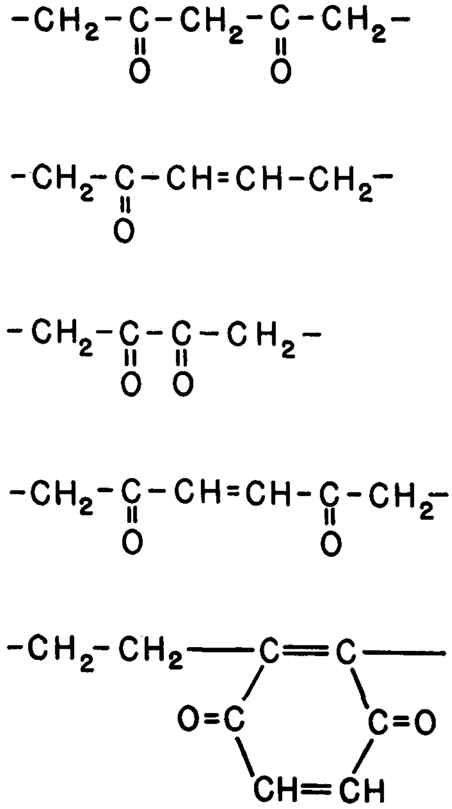

FIG. 3

The relative importance of the problems I have discussed, or any others, depends upon one's point of view. So far as the protective coatings industry is concerned, the importance of many drying oil problems can be diminished by blending or copolymerizing non-drying polymers with the drying oils. This however does not constitute a solution to the problems but rather an avoidance of them. To the manufacturers and suppliers of drying oils, who are naturally interested in seeing their product as widely used as possible, the unsolved problems will continue to be a most important challenge.

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