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Mechanism of drier action
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MECHANISM OF DRIER ACTION

AG 27'53

Introduction:

While many papers have been published relating to the effects of metallic ion catalyst on films of drying oils and resins, most of them have been limited to descriptions of the observed phenomena rather than to explanation. The reason for this can unquestionably be attributed to inadequate fundamental information relative to the oxidation of simple systems. Within the past ten years, such information has become increasingly available and it is the purpose of this paper to suggest one possible way in which some of the physical aspects of drier action may be correlated with existing facts. It will also be shown that the existing information is seriously deficient from the physical chemist's point of view and some means for remedying this situation will be suggested.

The Film Formation Process:

Those aspects of drier action which are of importance to the paint industry actually comprise a subdivision of a much broader topic - that of film formation. While the intricate details of organic chemistry which have been discussed in the preceding paper are of vital importance to a knowledge of the film forming process, many of the observed phenomena and properties of films can only be explained in terms of physical processes. For example, diffusion of oxygen into the film, migration of unpolymerized material throughout the film and other similar processes must exert a major influence on such properties as drying time, hardness, wrinkling, etc. It seems likely that very often these physical processes are the rate controlling steps which actually determine the course which the organic reactions will take and it is within the framework of this picture that the action of driers must be discussed.

Existence of a Polymer Distribution:

One of the best known phenomena of drying oil films is the fact that drying (i.e. solidification) usually occurs first at the surface with the formation of a "skin" which then proceeds to thicken until the material has become apparently solid throughout its depth. However, if such an apparently solid film is stripped from its substrate and extracted with an organic solvent it will be found that considerable unpolymerized material remains. Also, the ~~quality~~ quantity of extractable material decreases as drying time (or baking) is prolonged beyond that just sufficient to produce an apparently solid film. These observations lead to the concept of a polymer distribution of the type shown in Figure 1.

Presented before American Chemical Society, Chicago, Sept. 6-11, 1953

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Origin of the Distribution:

While the concept described above is probably familiar or at least acceptable to most chemists the precise sequence of events which is responsible for the distribution required more detailed analysis. The first step in the process must be the diffusion of oxygen (from the air) into the freshly deposited layer of oil or resin. Since experiments have shown that diffusion of oxygen into organic liquids is a slow process, the conditions exist for the formation of a distribution, or gradient, of oxygen within the liquid layer of oil. Further, since the source of oxygen is at the surface, its concentration will be greatest at the surface and, in general, the form of the gradient throughout the film will resemble the curves already drawn for polymer distribution in Figure 1.

The second step is the reaction of the dissolved oxygen with monomer (RH) via a chain mechanism to yield a hydroperoxide (ROOH) (1). Now, since Bolland (2) has shown that the rate of formation of ROOH is proportional to oxygen pressure at the low concentrations which must exist within the film, it follows that a distribution of ROOH will arise analogous to that of oxygen.

The final step of course is the conversion of ROOH to polymer via the intricate processes already described by Mr. Mueller (3). Again, the rate of conversion is related to the amount present and so the original gradient of oxygen concentration within the film is maintained through a long sequence of steps to result in the polymer distribution mentioned previously.

It must be admitted that the above description represents a vast simplification of the interrelation between the processes which produce the polymer distribution. For example, it may be pointed out that the polymer distribution curve is not likely to be identical in shape with that of either the hydroperoxide or oxygen. While there is undoubtedly a one-to-one correspondence between the various distribution functions the detailed and exact relationship is dependent upon the reaction kinetics of all the intermediate steps.

Forms of Distribution:

In view of the relationship between the shape of the distribution function and the reaction kinetics it follows that the form of the function will depend upon the chemical nature of the system as well as upon all physical conditions which influence relative rates of the intermediate reaction steps. While these relationships are too complex for detailed analysis at the present time, it is possible to infer the major effects in a qualitative fashion. Thus, the two principle chemical processes which determine

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the distribution are the formation of hydroperoxide and its decomposition to polymer. At the beginning of the oxidation reaction the rate of ROOH formation will always exceed that of decomposition. In the case of bulk reactions where the reactants are well stirred the rate controlling effect of oxygen diffusion is eliminated and a steady state of oxidation is eventually attained such that the rate of ROOH decomposition (i.e., the rate of polymer formation) equals its rate of formation (1). In the case of drying films, however, an important part of the drying process may occur before the steady state is reached and under such circumstances the ratio

$$\frac{\text{Rate of hydroperoxide formation}}{\text{Rate of hydroperoxide decomposition}} = \frac{R(f)}{R(d)}$$

determines the nature of the distribution.

The reason that this ratio constitutes a measure of the polymer distribution can be seen from the following: there will be no polymer gradient if no oxygen gradient exists. Similarly, no polymer gradient will be present if no hydroperoxide gradient forms. The rate of polymer formation depends on the rate of hydroperoxide decomposition. It has been shown that this rate is proportional to the hydroperoxide concentration which is in turn dependent on the rate of formation. Thus, the rate of polymer formation is dependent on both these rates, and a satisfactory explanation of the polymer distribution can be obtained from a consideration of the relative rates of these processes, i.e., the ratio R(f)/R(d).

For example, if R(d) is negligible compared to R(f) then the concentration of ROOH will increase with time somewhat as shown in Figure 2. The leveling of the distribution as time proceeds is due to the gradual disappearance of oxidizable groups at the surface. However, if R(d) is comparable to R(f) then ROOH distributions of the t_3 type (Figure 2) will never have a chance to form and the decomposition of ROOH will therefore occur while its distribution still resembles t_1. Thus, when R(f)/R(d) is near unity a steep polymer distribution should result while if the ratio is very large a more level distribution will be formed as shown in Figure 3. The physical properties and behavior of the film during the drying period must inevitably depend upon the nature of the distribution which exists during this time. Thus, a steep distribution (Figure 3, curve A) may be expected to result in a film which is tack-free while a large quantity of low molecular weight material still remains between the skin and the substrate. On the other hand a distribution of the type

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shown in Figure 3,B should result in a film which does not become tack-free until it has polymerized (hardened) throughout.

An even more significant property of drying oil films is their ability to wrinkle under certain conditions. The relationship between wrinkling and the distribution function may be deduced with the aid of two simple assumptions. First, it has been postulated that wrinkling is caused by swelling of a supernatant layer of polymer by the slow migration into it of monomer from underneath (4). Other effects undoubtedly contribute to the swelling - wrinkling phenomenon but experimental evidence strongly supports the monomer migration hypothesis. Secondly, it may be assumed that wrinkling cannot occur until or unless the distribution of polymer meets two specific conditions: (a) the concentration of n-mer at the surface must be great enough to confer solid-like mechanical properties on the upper layer and (b) the ratio of n-mer to material of lower molecular weight must be less than some specifiable value. If these conditions are accepted, it follows that distribution A (Figure 3) should wrinkle at a lower thickness than distribution B. In view of the fact that the film thickness required for wrinkling is an easily measured quantity, this property is at present one of the best available methods for estimating the nature of the polymer distribution.

Influence of Driers:

In the preceding sections it has been shown that the properties and behavior of a drying film depend upon the polymer distribution which result from the oxidation reaction. It has also been shown that a sharply peaked distribution results from factors which produce an R(f)/R(d) value near unity while a broad distribution must result from factors which yield a high value of this ratio. The influence of driers may now be inferred by examining the ways in which they affect R(f) and R(d).

Review of the Literature:

Since an excellent review has already been given in the preceding paper it will only be necessary to summarize those points which are of immediate concern in the present ~~agreement~~ treatment. Thus, it is generally agreed that the steady rate of oxidation is independent of metal-ion concentration; this statement also implies that the steady rate is independent of the type of metal ion. (Figure 4) It appears that the principal role of driers is to catalyze the decomposition of hydroperoxide (Figure 5). A high rate of decomposition generally results in an oxidation rate with a short induction period and a low steady state concentration of hydroperoxide. Conversely, slow rates of decomposition give long

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induction periods and higher steady concentrations of hydroperoxide (5). These relationships may be summarized in the following equations:

$$\frac{-dO_2}{dt} = K_1 (ROOH)^m (M{+}{+})^n (RH) \qquad (1)$$

$$(ROOH)_{steady)} = \frac{k_2}{(M{+}{+})^n} (RH)^2 \qquad (2)$$

$$\text{and } \frac{(-dO_2)}{(dt)_{max.}} = k_3 (RH)^2 \qquad (3)$$

where oxygen diffusion is neglected.

Effect of Driers on the Polymer Distribution:

It may be concluded from the foregoing that a wide range of effects due to variation in drier type and concentration may be expected. Thus, a drier type or concentration which yields a long, gradual induction period is one in which the R(f)/R(d) ratio is held greater than unity throughout a considerable portion of the film forming period. According to the reasoning given previously this should result in a distribution of the broad or flattened type. Conversely, a drier type or concentration in which the maximum rate of oxidation is reached very quickly should give a R(f)/R(d) ratio of unity throughout most of the film formation period and thus a sharply peaked polymer distribution.

It should be emphasized that this picture of drier action does not necessarily imply that R(f)/R(d) is a monotonic function of drier concentration in the time range prior to attainment of the steady state. The possibility of irregularity would appear to increase with the complexity of the oxidizing system since, as in the case of natural oils, a large variety of hydroperoxides exist, each of which has its own characteristic R(f) and R(d. As a result it may be expected that some film properties may experience maxima or minima as drier concentration is varied. This can result if the rate controlling step is changed from the diffusion of oxygen to the formation of hydroperoxide.

However, even the complexity introduced by this situation seems inadequate to explain the behavior pattern of certain metal ions. For example, copper and lead are known to possess weak drying action as compared to equivalent concentrations of cobalt or manganese. It might be supposed therefore that some concentration of copper (or other weak drier) could be found at which the drying behavior would be identical in every respect with a smaller concentration of cobalt. In practice, however, this supposition is

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not always borne out and, indeed, the deviations which exist in certain cases throw considerable doubt on the generality of equations 1-3 as well as upon the simple relationship which was previously suggested between R(f)/R(d) and the polymer distribution. The possibility of interpreting such anamolous behavior in terms of oxidation retardation mechanisms and variability in the chain termination processes has been suggested by Bawn (6), and George and Robertson (7). Unfortunately, the experimental data on these anomalous systems are inadequate even as a basis for speculation.

Future Research:

It would be not only extremely difficult but highly presumptuous to claim that a complete and infallible program could be outlined here which would result in the speedy solution of existing problems relating to driers. Indeed, it appears that many aspects of the problem, particularly in the realm of organic chemistry, are currently being pursued by such able investigators that no improvement could be suggested anyway. There are, however, a few simple varieties of measurements, which some of the foregoing conjectures suggest as meriting special attention. For example:

1. Oxygen consumption should be measured as a function of time, temperature and metal ion concentration for every metal considered useful in drying oil and resin systems. These experiments should be conducted first on a simple hydrocarbon such as tetralin, and later on a polyunsaturated material such as ethyl linoleate. Solutions should be used in preference to the pure olefin and stirring should be adequate to eliminate the rate controlling effects of oxygen diffusion. Results of these measurements should be plotted as shown in Figure 5 from which the steady rate of oxidation and other kinetic relationships may be calculated.

Measurements of this type have, of course, been reported in the literature but unfortunately the metals studied have been limited to only a few of the commonest "well behaved" driers while those reputed to give irregular behavior in film formation such as copper, lead, iron and the rare earths, have received little or no attention.

2. Hydroperoxide decomposition should be measured under non-oxidizing conditions, using the same list of metals selected in #1 above. Results should be plotted as in Figure 6 and kinetic relationships such as activation energy, steady concentrations of hydroperoxide, it should be calculated.

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3. Attempts should be made to observe and measure directly the concentration of gradients of oxygen, hydroperoxide and polymer (or other decomposition products) which arise in the diffusion-controlled oxidation. This type of experiment may require some uncommon techniques but it should not be extraordinarily difficult.

Summary:

It has been shown that the distinguishing feature of oxidation in a stationary film is the development of concentration gradients or distributions of oxygen, hydroperoxide, monomer and polymer. These distributions arise through the rate controlling effect of oxygen diffusion and are responsible for the observed properties and behavior of the films during the drying period. Differences between oxidizing systems, catalysts, etc., are attributed to variations in relative reaction rates of intermediate steps in the oxidation process which are capable of producing distribution functions of varying shapes. A qualitative argument was given to indicate the general nature of the relationship between the distribution shape and the known kinetics of certain common systems. Finally, it was pointed out that a quantitative argument of the same type would require additional information of specific nature and means for obtaining this information were suggested.

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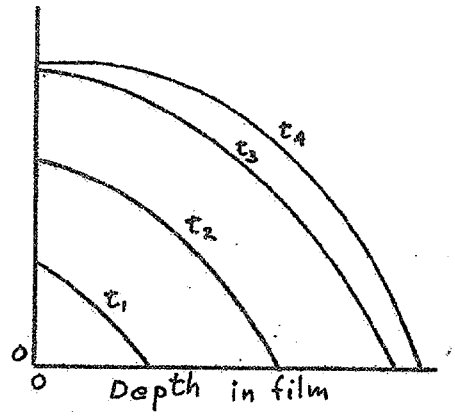


Fig. 1

Distribution of polymer at four different times in a film of thickness (x). Concentration is expressed in terms of percent material having degree of polymerization equal to (n). The shapes of the curves are schematic and may not resemble real distributions.

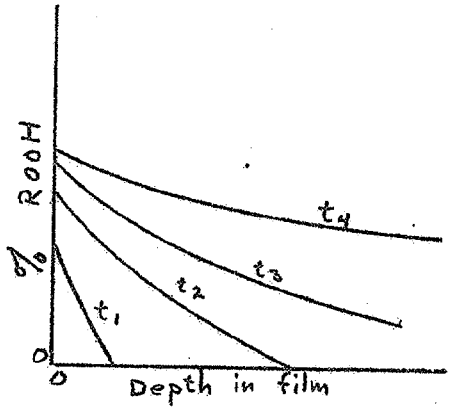


Fig 2

Distribution of hydroperoxide at four times in a film of thickness (x).

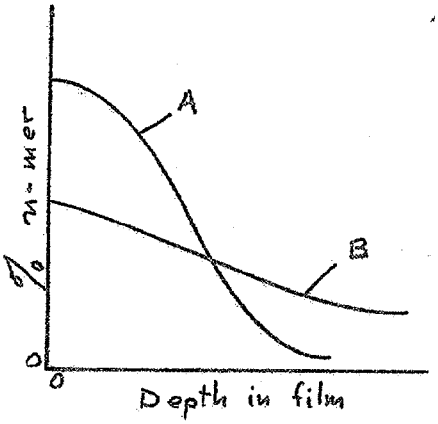


Fig. 3

Schematic representation of two widely differing types of polymer distribution curves.

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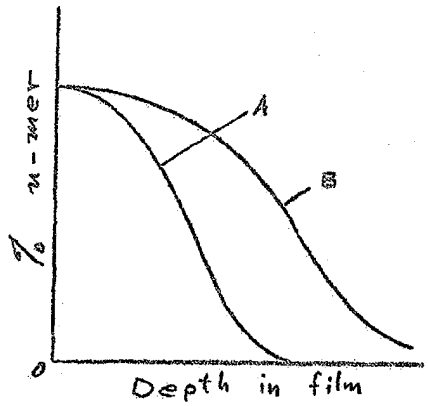


Fig 4

An example of two polymer distributions which would be expected tow rinkle at different thicknesses, i.e., (A) should wrinkle at lower thickness than (B).

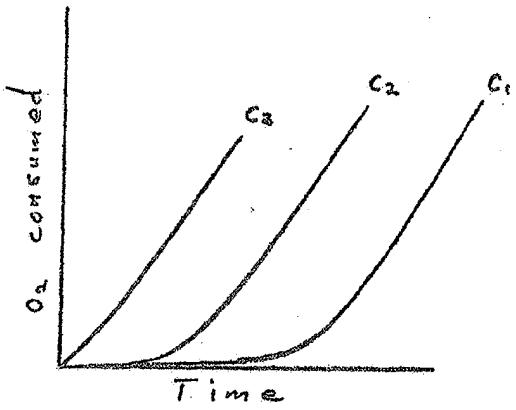


Fig 5

C_1, C_2 & C_3 indicate three different drier concentrations or three different driers at the same concentration.

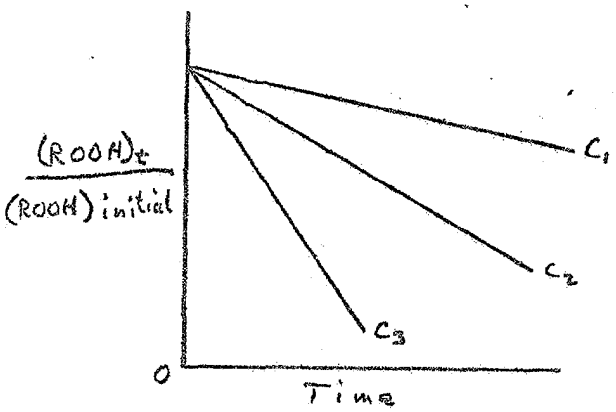


Fig 6

Decomposition of hydroperoxide under non-oxidative conditions at three drier concentrations.

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