lished, successful or unsuccessful, be brought together in a more usable form.

Third, a comprehensive program of fundamental research on drying oils should be initiated, including the following phases:

1. a thorough investigation of the basic chemistry of drying oils;
2. use of this knowledge of the basic chemical composition of drying oils as a starting point for research in the chemical modification of oils;
3. utilization of the materials developed through chemical modification of oils to formulate new products that will serve more effectively as raw materials in established uses or that will find a market in entirely new uses;
4. as an important corollary to the program of research on the drying oils themselves, the undertaking of studies, based on fundamental physical and chemical knowledge, to determine the mechanism by which oil films dry and the factors that affect color retention in protective coatings; and
5. the intensification of long-term breeding research on the agricultural plants from which oils are derived.

We are firmly convinced that the carrying out of the above recommendations will contribute materially to improving the present competitive position of the drying oils in the American economy. We are even more firmly convinced that there will be a continued steady decline in the use of drying oils from agricultural sources unless important new discoveries are made in the fields of research outlined above.

In closing we would like to make one further observation that seems pertinent to this discussion. The initial comment received from many of the drying-oil consumers, when they were asked to cite difficulties with drying oils, amounted to: "We don't have any special problems with oils. We have troubles with them, of course, but we know what they will and won't do and we just accept them as they are." This statement, and the frequency of its occurrence, would indicate that many drying-oil consumers have pretty much resigned themselves to taking the oils as they come, with little hope that they will get any better. Such an attitude, on the one hand, is a virtual invitation to synthetic-materials manufacturers to keep supplying new products that will give the drying-oil consumer less trouble and better results. On the other hand, it should serve as a ringing challenge to the drying-oil-producing industry, the Department of Agriculture, and all others interested in these oils to do all that can be done to develop new raw materials that will be received with greater enthusiasm by producers of paint, varnish, floor coverings, and other products.

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II

Autoxidation and Oxidative Polymerization[1,2]

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IT IS WELL recognized that the fundamental chemical basis for the use of drying oils in protective coatings and related applications consists of autoxidation of the drying oils at the unsaturated centers in the fatty acid chains and a subsequent linking together of the fatty acid chains by polymer-forming reactions.

It is not nearly so well recognized however that the presence of unsaturation, and that oxidation at the unsaturated centers, are responsible not only for the strong points of drying oils as film-formers but also for some of the weaknesses that have played a role in the displacement of drying oils by other types of film-forming materials.

Solutions to some of these problems must be found through fundamental chemical research. One of the prime objectives of such research must be to determine how to exploit to the fullest the desirable film-forming reactions based on oxidation at the unsaturated centers, and at the same time minimize, or even eliminate if possible, undesirable changes such as yellowing and other forms of film degradation, which also result in large measure from oxidation at the unsaturated centers.

This is essentially the direction that has been taken, whether consciously or unconsciously, in the development of such vehicles as alkyds and other drying oil derivatives, without which the drying oil industry would have suffered even more than it has. The introduction of phthalic anhydride into oils permits polymer building *via* ester linkages as a partial substitute for the functionality that must otherwise be provided by the unsaturated fatty acids radicals. Thus, in alkyds, oils with lower total unsaturation may be used. Because fewer unsaturated centers are needed for film-formation, fewer unsaturated centers will also be available for degradative oxidation reactions.

In this brief presentation an avenue of research will be suggested that has not been explored appreciably and that could provide much useful information on how to exploit intelligently the desirable aspects of oxidation at unsaturated centers, and at the same time permit reduction in the undesirable aspects. Before doing this however, it may be well to summarize very sketchily the more important points that are known about autoxidation and oxidative polymerization.

Conjugated fatty acids, such as eleostearic acid in tung oil, and the conjugated diene acids in dehydrated castor oil, possess actual polymerization functionality before being oxidized in a drying film. Oxidation is therefore not needed to produce polymerization functionality but instead serves to produce the peroxides that are needed as polymerization catalysts. Tung oil and dehydrated castor oil, although important, are a relatively small part of the drying oil industry from the standpoint of volume, and we shall not consider them further at this time.

The important drying oils are those that contain appreciable proportions of unconjugated polyunsaturated fatty acids. The mono-unsaturated acid, oleic acid, and saturated acids oxidize only very slowly and, even when oxidized, do not acquire any appreciable polymerization functionality.

Linoleic, linolenic, and other polyunsaturated acids, although possessing no actual polymerization func-

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[1] Hormel Institute publication no. 119.

[2] Presented at the fall meeting, American Oil Chemists' Society, Minneapolis, Minn., Oct. 11-13, 1954.

tionality in an unoxidized condition, acquire such functionality upon autoxidation. It has been found that the principal reaction involved in the autoxidation of the polyunsaturated centers is a formation of peroxide and the simultaneous shifting of a double bond to produce a conjugated diene. When a sufficiently high concentration of conjugated diene has developed, polymerization takes place.

The mechanisms involved in the polymerization reactions and the structures of the products formed are not well understood, and these constitute a very large and potentially fruitful field for research in themselves. Important as the nature of oxidative polymerization reactions may be, it is not the area that will be emphasized in this presentation.

The Federation of Paint and Varnish Production Clubs has recently completed an extensive program of research on film-formation, employing a number of special vehicles and several ordinary commercial vehicles. The special vehicles included a series of glyceryl, pentaerythrityl, and dipentaerythrityl esters of pure oleic, linoleic, and linolenic acids.

Pure oleate esters failed to form solid films. Even though they did slowly oxidize, oxidation failed to impart any appreciable polymerization functionality. The linoleate and linolenate esters readily yielded hard films, but, in general, the films were inferior in all cases to ordinary linseed oil films in such characteristics as resistance to weathering, resistance to yellowing, gloss retention, water- and alkali-resistance, and adhesion. Of the important properties ordinarily desired in films for most purposes, only the speed of drying of the special vehicles was satisfactory.

What was the reason for the poor performance of these pure esters of linoleic and linolenic acids? At least a partial answer is found if one compares the average functionality per molecule needed to give hard films with the total potential functionality actually present in the form of unsaturated centers in the fatty acid chains. The studies of the drying of the pure linoleate esters revealed that setting of the films occurred when approximately two linoleate groups per molecule on the average had participated in the polymerization reactions. All of these compounds however contained three or more linoleate radicals. Since only two linoleate radicals on the average appeared to be needed, the extra linoleate radicals were largely superfluous.

Not only were they superfluous, but they were also points of weakness in the set film. To a large degree they were prevented by the setting of the film from participating in polymerization reactions. Nevertheless they were subject to oxidation, and the oxidative degradation that occurred at these points undoubtedly contributed directly or indirectly to early breakdown of the films.

It is desirable to emphasize that, on the average, approximately two functional groups per molecule were needed for film production. An oil consisting exclusively of bi-functional molecules would yield only linear polymers and thus would not develop insoluble three-dimensional structures. Some tri-functional molecules are needed for cross-linking. On the other hand, some mono-functional and zero-functional molecules may be needed as internal and external plasticizers to achieve the most desirable film properties.

These thoughts then point to a type of research that is very much needed, namely, research to ascertain what proportions of molecules with various degrees of functionality in the form of polyunsaturated centers will give films with good physical properties, without at the same time leaving appreciable quantities of unsaturated centers that can only undergo oxidative degradation.

Natural oils, such as linseed oil, consist of mixtures of molecules with various potential functionalities that make them superior to pure synthetic oils with excessive functionalities such as trilinolenin, or PE tetralinolenate. There is no assurance however that the proportions of molecules with various functionalities in linseed oil or other oils are ideal. On the contrary, there are various lines of evidence which suggest that marked improvements could be made.

It has long been recognized that the composition of oils in terms of component fatty acids is important to the properties of films. What is not so generally recognized, and what has been emphasized here, is that oil composition, in terms of the proportions of molecules with various functionalities, is also very important.

Once fundamental information has been obtained in this area, it is probable that much can be done to improve oils more intelligently by solvent segregation methods and chemical modifications, such as are already practised to a considerable extent on a purely empirical basis, and by plant-breeding methods.

To summarize, fundamental information about the most favorable compositions of oils or modified oils is needed so that the modification of oils may be directed more intelligently toward the most favorable compositions.

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III

Unsolved Problems in the Modification of Drying Oils

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THE MODIFICATION of drying oils so as to improve their properties for a given application constitutes one approach toward maintaining or improving their position as raw materials for coatings, floor coverings, etc. As evidence of this is the fact that modified drying oils have been and are of commercial importance, for example, maleic modified soybean oils as outside house paint vehicles. This particular application points up one problem, namely, that when some principle of modification of a drying oil is developed, it can in general be applied to one drying oil as well as another, and the net result may be to replace another drying oil. Thus when a certain relative price situation exists, maleic modified soybean oil will to some extent replace linseed oil in outside house paints.