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

ROBERT L. TERRILL, Spencer Kellogg and Sons, Inc., Buffalo, New York

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.

Also the remote possibility that drying oils *per se* would recapture a large portion of the markets they have lost has been noted in the keynote talk. Certainly in this discussion it is not meant to imply that modification of drying oils could improve their properties sufficiently so that the older type of interior paints, wherein essentially all of the vehicle was oil, would come to be of importance again; here the problem is primarily economic. In this connection it must also be noted that the modification of drying oils generally leads to some resinification and is accompanied by an increase in viscosity, necessitating the use of thinners and resulting in the use of less oil. In fact, about the only way one can differentiate some modified drying oils from materials otherwise known as resins is by their physical state. For the purposes of this discussion we shall adopt a very broad view of the modification of drying oils.

The modification of drying oils can be arrived at in one of several general ways. Let us discuss the problems in the various general classifications and certain specific applications. First, of course, modification of drying oils can be attained by various physical or chemical segregation processes. In recent years, and particularly in England, much has been learned about the basic composition of drying oils, and a considerable amount is being published right along. Of considerable interest in this connection is the new Craig countercurrent extraction apparatus now operating at the Northern Utilization Research Branch at Peoria. The point is, of course, that without accurate fundamental knowledge of what one is trying to separate, it is rather difficult to decide how to go about it. However it must be admitted that the presently available physical segregation processes are reasonably efficient as regards technical operation and that the problem is basically one of cost, specifically that of obtaining the fractions having given properties at a relatively low cost. Certainly more problems exist in the field of chemical separation, the surface of which has as yet only been scratched. The possibilities of chemical complexing (as exemplified by urea fractionation) remain largely to be explored.

Another aspect of the fractionation or segregation of dryings oils concerns the effect and utilization of minor constituents that are present. Here again the problem is at least partly economic since it does seem that utilization research which will increase the value of minor constituents of drying oils would be worthwhile.

ANOTHER APPROACH to the modification of drying oils is by thermal or catalytically induced chemical changes in molecular structure. In the field of polymerization, of course, there has been a considerable amount of fundamental work. While polymerized oils *per se* are not modified drying oils of improved properties, they do have some very desirable qualities which could well be emulated in other materials, synthetic or modified as the case may be. However the field of catalytic polymerization is well within the scope of modified drying oils, and in this field there are certainly some unsolved problems. These would have to do principally with the low temperature catalytic polymerization with boron fluoride derivatives, etc. There is a considerable amount of published information concerning catalytic polymerization with boron fluoride, etc., but not very much of it is at all fundamental in nature and such catalysis has had limited commercial application.

Drying oils can be modified by inducing conjugation therein, and the means are at hand for doing this by several processes, including nickel catalysts, organic peroxides, sulfur dioxide, and anthraquinone derivatives. However, while the processes are at hand, in the case of most drying oils the resulting products have serious deficiencies, principally an after-tack which is especially pronounced in conjugated linseed and soybean oils. While a faster polymerization rate can be attained more economically by catalysts of the aromatic poly-nuclear type, some of the other properties of conjugated oils are very desirable, such as their fast set and drying time, hence some understanding of the cause of the after-tack noted might lead to a cure. There has been some research, and solutions for this problem have been suggested, but it has not yet been solved.

Modified drying oils can be produced by interesterification, as in the relatively simple instance where soybean oil and Chinawood oil are heated together in the presence of a catalyst and an exchange of fatty acid radicals takes place between the various triglycerides present. The production of polyvinyl esters by ester interchange has already been discussed at this symposium. There are probably more good sound data applicable to modification of drying oils available in this field of endeavor than in any other. It has been a fruitful field in edible oils, and its utilization in the modification of drying oils is chiefly a problem of application of existing knowledge.

ANOTHER GENERAL MEANS of modifying drying oils is by functional modification by addition, condensation, and copolymerization reactions. The reaction of drying oils with reactive hydrocarbon or substituted hydrocarbon monomers has been of some commercial importance. Providing the answers to certain problems can be found, this approach could result in products potentially cheaper than alkyd resins and having generally similar and in some cases superior properties. The study of such copolymerization is basically a study of the activity of the fatty acid double bonds; in simplest terms the main problem is how to cause a reaction between the relatively sluggish fatty double bonds and those of the extremely active monomers. These latter much prefer to react with themselves long before the activation temperatures for fatty double bonds are achieved. A thorough investigation of catalysts immediately suggests itself and indeed may ultimately prove fruitful, but the answer is not so simple since the monomers respond to catalysts, and consequently polymerize, much more readily than do the double bonds of drying oils. There are unsolved problems in copolymerization of drying oils with diene monomers, such as cyclopentadiene. In fact, there is substantially no chemical literature on this point. The products in this case have certain serious deficiencies, principally a tendency toward brittleness and continued embrittlement which might well be overcome were the nature of the resultant polymers better understood. In the field of vinyl copolymers there is of course a tremendous literature on styrenation and styrene copolymers. It might well be argued that since so much work has been done, then styrene copolymers should be of much greater importance than 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]

E. B. FITZGERALD, Marshall Laboratory, E. I. Du Pont de Nemours and Company, Philadelphia, Pennsylvania

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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