amounts of sodium ions. When these materials are used in hard water the observed minima in deposition (or maxima in whiteness of swatch) are a consequence of the stoichrometric titration to form the Ca or Mg complex followed by the normal increase in deposition due to added sodium ion.

3. Soaps remove divalent ion by precipitation, and thereafter the deposition due to salt effect is small.

4. CMC inhibits soil deposition in the presence of mono- as well as polyvalent ions. It does not sequester or remove calcium ion to any marked degree. The amount of CMC required for protection is relatively small.

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REFERENCES

1. Vitale, P. T., J. Am. Oil Chemists' Soc., *31*, 341 (1954).
2. Nieuwenhuis, K. J., J. Polymer Sci., *12*, 237 (1954).
3. Bartholme, E., and Buschman, K. F., Melliand Textilber., *30*, 249 (1949).
4. Thompson, W. E., J. Am. Oil Chemists' Soc., *26*, 509 (1949).
5. Ross, J., Shedlovsky, L., and Jakob, C. W., J. Am. Oil Chemists' Soc. (in press).
6. Vaughn, T. H., and Smith, C. E., J. Am. Oil Chemists' Soc., *25*, 44 (1948).

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Panel on Drying Oils

I

Research, the Key to Future Markets for Drying Oils[1]

ODIN WILHELMY JR. and HARRY W. BARR JR., Battelle Memorial Institute, Columbus, Ohio

UNDER A CONTRACT with the U. S. Department of Agriculture the Battelle Memorial Institute recently completed a year-long survey of the market potential for fats and oils in drying-oil uses. The report of this study will be published by the Department later this year or early in 1955. However John Cowan, of the Northern Utilization Research Branch, Agricultural Research Service, Peoria, Illinois, and Shelby Robert, of the Market Development Branch, Agricultural Marketing Service in Washington, under whose general direction this study was made, have given us permission to give you a preview of the report.

We feel that it is particularly appropriate for the initial report on this study to be presented before this Society. Several members contributed personally to the project by talking with us last winter and thus have a special concern with its outcome. All, we believe, will have an interest in the results because they bear rather closely on the future prospects of the industries that process and consume drying oils.

This study had its inception early in 1953. At that time the U. S. Department of Agriculture was becoming increasingly concerned by the sizable stocks of linseed oil in its custody, the decline in prices of most fats and oils, and the shrinking market for inedible fats and oils in drying-oil products. The Department was further concerned that the continuing shift by the using industries to petroleum derivatives, rubber-base paints, and synthetic resins in lieu of drying oils might portend a critical position for drying oils from agricultural sources.

Recognizing these problems, the Department outlined a study aimed at finding out a) the factors affecting the use of various fats and oils in the drying-oil industry, b) the difficulties being encountered by users of drying oils and the modifications desired to make the oils more useful in these industries, c) the reasons why synthetic materials, non-oil paints, and tall oil are capturing a larger share of the protective-coatings market, d) the price and supply conditions under which one drying oil might be substituted for another, and e) the present and probable future supply and price situation for materials used in the production of the synthetics which are replacing drying oils. It was felt that this information would put the Department and the drying-oil industry in a position to take more effective action, particularly in terms of marketing and technical research, toward maintaining or improving the position of agricultural drying oils in competition with non-fat products.

It should be apparent from this brief review of the objectives of the study that the primary aim of the project was to gather information and ideas that would ultimately benefit the farmer-producer of the crops from which drying oils are obtained. It necessarily follows however that any knowledge of how to process and use drying oils more effectively would also be of benefit to the industries that supply these oils or consume them in their manufacturing processes. It should further be pointed out that while our report suggests a general research approach that may help to overcome some of the problems of the drying-oil industry, it does not spell out the particular chemical or physical research techniques that should be employed. The determination of specific experimental techniques rests more properly with technical men who work with these oils in the laboratory the year around.

In setting up our survey, it was decided that personal interviews with key men from selected companies in the drying-oil industry would be the most effective method of gathering the needed information. In order to get a good cross section of opinion, interviews were sought and completed with 46 paint, var-

[1] Presented at the Paul Bunyan Meeting of The American Oil Chemists' Society, October 12, 1954, Minneapolis, Minn. A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Market Development Branch of Agricultural Marketing Service and Northern Utilization Research Branch of Agricultural Research Service.

nish, or lacquer manufacturers, 15 other major users of drying oils, 11 producers of synthetic resins or basic raw materials for them, nine oil suppliers, eight trade associations, and two government laboratories. Officials of the leading companies in each of these fields and of a selected group of smaller companies were interviewed. Geographically, these companies ranged from Boston to San Francisco and from Montreal to Chattanooga. From a product standpoint the opinions of manufacturers of nearly all types of drying-oil-containing end-products are represented in the survey, as are suppliers of drying oils and synthetic raw materials and producers of intermediate products utilizing these materials.

The successful completion of the survey stems in large measure from the very fine cooperation given by the companies and representatives contacted. More than 90% of the interviews sought were actually completed. Representatives of the Department of Agriculture provided helpful counsel and guidance throughout the study. Special mention must also be given to the National Pant, Varnish, and Lacquer Association, whose officials very generously gave support, advice, and encouragement to this undertaking.

EXCEPT for necessary background and descriptive material the report submitted to the Department of Agriculture contains three major sections: one on current patterns of drying-oil use, a second on probable future trends in that use, and a third covering present technical difficulties and needed research to overcome those difficulties. In other words, it indicates what has been happening in recent years, and why; what is likely to happen in the near future, and what types of research might, if successful, materially alter these future trends.

Not too much of what is in the report can be considered "new" or "different." There may be many observations to which your reaction will be, "Oh, I knew that all the time." The report however is "new" in the sense that it brings together in one place the knowledge and opinions of men from all segments of the drying-oil industry. As such, it can be looked upon as an industry-wide opinion on the probable future of the drying oils and the most pressing needs in the field of drying-oil research. In that sense, it is *your* report to the Department of Agriculture and the drying-oil industry, informing and advising all concerned in order that fats and oils from agricultural sources can be used to maximum advantage and possibly improved.

An understanding of recent trends in drying-oil usage and of the reasons underlying those trends was considered basic to the other phases of our research effort. The years 1949 and 1952 were selected as base years, and information was gathered and analyzed on changes in formulation practice and raw-material use patterns within this period.

As you are undoubtedly aware, significant changes in formulation practice did occur between 1949 and 1952 in the industries that consume drying oils, and many of these shifts are still in progress. One can single out four changes during this period that probably were the most important in terms of their effect on drying-oil consumption patterns.

The first of these was the introduction and widespread use of styrene-butadiene latex emulsion paints. Sales of latex vehicles in this country skyrocketed from an estimated 2 million lbs. in 1949 to about 40 million lbs. in 1952. A second major change was the increasing use of synthetic materials in the manufacture of both paint and non-paint products. In the protective-coatings field this period saw the introduction of silicone alkyd resins, interior flat alkyds, epon-modified oils and alkyds, polyvinyl acetate resins, and styrenated alkyds. Acrylic resin emulsions came into prominence in 1953. Similar developments occurred in the other drying-oil-consuming industries: the increased use of vinyl resins in making floor coverings and of various synthetic resins in the manufacture of table and wall coverings, to cite only two examples.

The third significant change was the growing use of tall oil and its derivatives in the production of both paint and non-paint products. The fourth was a shift from oleoresinous to alkyd-type vehicles on the part of the smaller paint companies, a shift that had been largely completed prior to 1949 in the bigger companies.

Why did these changes in formulations take place? Most of them occurred because the resulting end-products were of higher quality or possessed properties superior to those attainable from previously used formulations. Some of them were made because less expensive raw materials could be used to make equally good or better products. Latex paints achieved widespread acceptance and popularity largely because of their ease of application and clean-up, combined with effective promotion on the part of the manufacturer. Other synthetic materials, in many cases "tailor-made" for specific applications, imparted properties to end-products that simply could not be achieved with drying oils, properties such as improved durability, better chemical or heat resistance, or faster drying time. Tall oil, as well as its derivatives, was used in larger quantities because it costs substantially less than vegetable drying oils and can be effectively used in combination with other oils to manufacture certain intermediate- and end-products. Production of alkyd resins continued to increase because they offered effective competition for latex emulsion interior paints and because they could be made from soybean oil, a less expensive ingredient than linseed.

Whatever the basis for a particular shift in formulation practice, the over-all end-result was a marked rise in consumption of synthetic materials in lieu of drying oils, and of soybean oil in lieu of linseed during the 1949-52 period. That pretty well covers developments in the drying-oil industry in the recent past, developments with which you are familiar.

LET'S TURN NOW to the future and see what appears to be in store there. It is the consensus of men with whom we talked that, unless a significantly greater research effort is applied to the drying oils, the following trends are likely in the future:

1. The use of synthetic raw materials in the manufacture of both protective coatings and non-paint products will continue to increase at the expense of the drying oils, with a resultant continued decline in drying-oil consumption. Since expansion in the total markets for most of these products is anticipated, the decline in drying-oil consumption as a percentage of total raw-materials usage is likely to be greater than the decline in actual volume of oils consumed. Unless there is a major decline in the price of drying oils as a group relative to tall oil, consumption of tall oil and its derivatives also seems likely to increase in the future, particularly if the quality of

these materials continues to improve as it has in recent years.

2. Consumption of soybean oil and soybean-oil fatty acids is likely to increase at the expense of linseed oil if soybean oil is cheaper than linseed, as it has been in past years, and if the popularity of alkyd resins continues. The market for linseed oil may see a further cutback within 10 years if the anticipated development of an exterior house paint of a non-linseed type becomes a reality.
3. In protective-coatings products average oil content will continue to decline in trade-sales and industrial-maintenance lines, but will remain relatively stable in industrial-product finishes. The net effect will be a decrease in the production of "exclusively oil" coatings, accompanied by an increase in production of both "part-oil" and "non-oil" coatings. Production of floor coverings will continue to increase, but most of the increase will be in the form of vinyl-based coverings and other types in which relatively little oil is used. Prospective production trends for other drying-oil-consuming products do not appear to offer any significantly greater market for drying oils. On the basis of relative market size and other factors, interior flat wall finishes and floor coverings appear to be the two products in which drying oils, if improved, might hope to regain lost markets. On the other hand, the present position of the drying oils in exterior house paints is likely to be in jeopardy within a few years unless research on linseed oil keeps pace with synthetics developments.

On the basis of the above predictions by themselves, one can scarcely have a very optimistic outlook about the future of drying oils. Fortunately for the industry, there is reason to hope that the trends mentioned may be moderated with respect to the over-all use of oils. The basis for this hope lies in a concerted research effort directed at modifying and improving drying oils so as to make these raw materials more attractive to their consumers. The possibility of drying oils, *per se*, recapturing a large share of the markets they have lost to synthetic materials is admittedly remote. Potentially however these oils might well serve as raw materials for making other film formers that would yield end-products with even better properties than those presently attainable only from synthetic materials. The fact that there has been no significant production from drying oils of a latex emulsion paint or a "steam-set" ink is no proof that such production is impossible.

In setting up this study, the Department of Agriculture fully recognized the promise that research might hold for drying oils. For this reason, major emphasis was given during the interview phase of the study to determining what are the major technical difficulties faced by both consumers and processors in their use of the oils, and the types of research that they felt might provide a solution to these problems.

Listed separately, the individual drying-oil problems cited by the men interviewed would total well over a hundred. Measured in terms of their frequency of occurrence however, this diversity of difficulties can be reduced to a relatively few major problems. Among protective-coatings manufacturers the two problems most frequently cited were speed of drying and color retention. The problems mentioned by other major consumers of drying oils were similar to those listed by paint producers although in a number of instances the specific film properties desired are at the opposite end of the scale. Most of the problems cited by drying-oil suppliers were of a fundamental nature. These companies would like to know more about the basic structure and composition of the oils, the mechanism of film formation, the effect of minor ingredients on film-forming properties, the results of reacting oils and oil constituents with various reagents, the possibilities of developing new products if oils are treated as chemical raw materials, and so forth.

Nearly all of the companies contacted are in favor of additional research on drying oils and look upon such research as the only real hope for maintaining or improving the competitive position of the oils. The companies further believe that the greatest need lies in the field of basic or fundamental research and that the Department of Agriculture can make its greatest contribution to the well-being of the industry by conducting fundamental investigations on the oils.

OUT OF THE multitude of problems and ideas on which research was recommended, we have selected those that appeared to be potentially most effective in improving the relative competitive position of the drying oils in future years. While these suggestions were directed to the Department in the report, it is felt that the drying-oil industry could well give serious thought to ways in which it can aid in the fulfillment of these recommendations. These major recommendations for future drying-oil research are given below.

First, there should be an increased recognition, in both policy-making and research-planning, of the potential value of drying oils as basic chemical raw materials. Implicit in this recognition and logically growing out of it would be three desirable developments that would serve to enhance the position of the drying oils: a) competitive prices for the drying oils which would make them attractive as raw materials for developing new or better products; b) stable prices for oils, thereby eliminating the factor of price fluctuation that tends to depress their use in some products currently and that would certainly make them less attractive as chemical raw materials; and c) adequate production without encouraging overproduction. Since the research that may enable the drying oils to recapture lost markets or find new markets will necessarily take considerable time to become an effective influence on drying-oil consumption, it follows that continued over-production in the years immediately ahead would be unwise. Reasonable levels of production for drying oils in this interim period would help keep the supply of the oils within bounds and increase the chances of finding adequate markets through research and development. The action necessary to bring about these developments must necessarily be determined by those persons responsible for formulating agricultural policy as it relates to drying oils.

Second, a research program should be established promptly in which all available sources of information on the results of previous drying-oil research would be thoroughly reviewed, screened, organized, evaluated, and widely disseminated among persons and organizations concerned with the production or consumption of drying oils. There is no question that a large amount of worthwhile research on drying oils has been conducted. However much of this research (within the industries that sell or use drying oils) has been inadequately publicized, resulting in a wasteful diversity, decentralization, and duplication of effort. Before an effective program of additional research on drying oils can be carried out, it is essential that the results of previous research, published or unpub-

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]

W. O. LUNDBERG, The Hormel Institute, University of Minnesota, Austin, Minnesota

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-

[1] Hormel Institute publication no. 119.
[2] Presented at the fall meeting, American Oil Chemists' Society, Minneapolis, Minn., Oct. 11-13, 1954.