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Semi-micro combustion, solvent extraction, and oleic acid adsorption of synthetic drying oils : part II.

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UNIVERSITY OF LOUISVILLE

SEMI-MICRO COMBUSTION, SOLVENT EXTRACTION,
AND OLEIC ACID ADSORPTION

of

SYNTHETIC DRYING OILS

PART II

A Thesis

Submitted to the Faculty

of the Graduate School

of the University of Louisville

in Partial Fulfillment

of the requirements

for the degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

ISADORE NATHAN COOPERMAN

June, 1949

AND OLBITIC ACID ADSORPTION

SYNTHETIC DRYING OILS

PART II

ISADORE NATHAN COOPERMAN

Approved by the Examining Committee

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ABSTRACT

The rates of oxidation, solvent solubility, and oleic acid adsorption, of natural and synthetic drying oil films were studied by semi-micro analytical methods.

The thesis consists of three phases:

- I. Ultimate analysis to determine the oxygen content of a film at specific time intervals.
- II. Extraction of the films to determine their solvent solubility as a function of time.
- III. Oleic acid adsorption to get a correlation of the structure of the film.

Seven materials were examined:

- ✓ A. Glyceryl Trilinoleate
- ✓ B. Pentaerythritol Tetralinoleate
- ✓ C. Pentaerythritol Oleate
- ✓ D. Pentaerythritol Oleic Acid Long Oil Alkyd
- ✓ E. Dipentaerythritol Linoleate
- ✓ F. Dipentaerythritol Linolenate
- ✓ G. Pentaerythritol Linolenate

Glyceryl Trilinoleate was found to absorb 28% oxygen in 4 days' time, and this amount remained essentially constant. Solvent insolubility reached 52% in 7 days and then increased gradually.

Pentaerythritol Tetralinoleate absorbed 26% oxygen in 7 days and then leveled off, while solvent insolubility attained 73% and then increased gradually.

Pentaerythritol Oleate did not dry and was as liquid three months after as when first brushed out.

Pentaerythritol Oleic Acid Long Oil Alkyd did not dry; and two months after it was brushed out, it was just becoming tacky.

Dipentaerythritol Linoleate absorbed 25% oxygen in 4 days, which then became essentially constant, while its solvent insolubility attained a figure of 75% in 2 days.

Dipentaerythritol Linolenate absorbed 26% oxygen in 2 days. Its insolubility was 80% in 1 day, and almost 100% in 7 days.

Pentaerythritol Linolenate was found to absorb 26% oxygen in 2 days and became almost 98% insoluble in 4 days.

The solvent used in all extractions was carbon tetrachloride which was found to give good results.

Dipentaerythritol Linolenate exhibited the phenomena of breaking up into strands, or fibers, on being extracted with carbon tetrachloride.

Oleic acid adsorption seemed to indicate that adsorption did not depend upon original chemical structure since the ratio of weight of acid adsorbed to weight of extracted film fell between the range of 1 to 1 and 1.5 to 1.

The method used for film formation involved the brushing out of the oil upon glass plates and weighing. Oil was brushed out over a given area, and for a certain thickness, was coated and weighed until the desired amount was spread on the glass plate.

Linseed oil data are presented for comparison purposes.

INTRODUCTION

Since its earliest development, the paint and varnish industry has been troubled by the unpredictable fluctuations in the price and quality of the raw materials used in the manufacture of its products. These disadvantages are readily apparent in the field of drying oils, where the majority of raw materials are of agricultural origin and, until the present time, have been largely imported.

Since no natural raw material is ever uniform, varying in quality with its site of origin, the weather conditions prevailing during ripening of the oil producing seeds, and the conditions extant during transport and storage, it is no wonder that the oil crushers in this country have found it difficult to maintain uniform quality, even under the best controlled conditions.

Moreover, the paint industry has been plagued by a problem common to almost all agricultural raw materials, that of varying cost and supply. Few items on the world market show more violent variations in this respect than do the drying oils. This can best be illustrated by reproducing a portion of a table (1) of comparative prices for natural and factory made materials over a period of several years.

	Natural				Factory Made			
	Linseed Oil		Tung Oil		Lithopene		Benzol	
	¢/#		¢/#		¢/#		¢/gal.	
	High	Low	High	Low	High	Low	High	Low
1932	7.0	5.3	7.8	5.8	4.5	4.5	20	20
1936	10.5	9.2	19.5	12.8	5.0	4.2	18	16
1939	11.1	8.5	28.0	13.8	4.8	4.1	16	16
1941	11.7	9.1	35.5	25.8	4.4	3.9	15	14
1945	15.5	15.5	38.4	38.4	4.8	4.3	15	15
1946	34.1	15.5	38.4	38.4	5.0	4.3	15	15

The reasons for these fluctuations are manifold and, to a large extent, uncontrollable. Crop failures reduce the supply for a given year and drive the price up, bumper crops reverse this position, and speculation aggravates the situation. Political upheaval in the main oil producing countries, such as China (Tung Oil) or Manchuria (Perilla Oil), and the monetary difficulties in the main oil buying countries, which includes almost all of Europe, are some of the many factors that increase the uncertainty of the world markets.

In addition, the fact that the natural drying oils have inherent structural disadvantages has increased the difficulties already burdening the industry. Even with the best of corrective measures, the natural drying oils are far from ideal since

- (1) they all contain fatty acids of the saturated or low-unsaturated type which have no drying value,
- (2) almost all contain the all-important double bonds in insufficient number and in unfavorable positions,
- (3) all are esters and therefore saponifiable with the result that in practical usage they are well resistant to alkali, and
- (4) the triglyceride structure of the natural oil molecule is only one of many possible ester structures and by no means the best.

With the beginning of hostilities in World War II, the paint and varnish industry was cut off from a major portion of its sources of raw material with which it produced the coatings essential to the war effort. This position was unbearable for an industry already overtaxed with difficulties, and means had to be devised to alleviate the situation. Thus were the chemists in this country presented with the problem of finding substitute materials that would do the job as well as, or better than, those originally used. Their progress in developing materials and methods was rapid, and many drying oils in use today may be attributed to their success (29). Dehydrated Castor Oil was one of the earliest

developments and will undoubtedly become permanent in its usage. Linseed and Soybean oil were modified and imbued with properties similar to those of dehydrated castor oil, namely, quick, hard drying, and fast polymerization. These are and will be used because of their very specific characteristics. And finally, some very highly satisfactory oils were produced, and are being produced, by substituting the glycerine with higher alcohols like pentaerythritol, sorbitol, manitol, etc. (17,21).

Nonetheless, understanding of the chemical changes involved in the drying process of these materials has not kept pace with the rapid rate that knowledge has been gained of their physical characteristics.

With the methods now available for producing synthetic drying oils, it became apparent that, before any further work should be done toward improving their chemical properties, or physical characteristics, a knowledge of the exact nature of the chemical changes involved in the drying process should be acquired.

This was the problem that prompted the Federation of Paint and Varnish Production Clubs, to study the physical and chemical properties of twenty-four selected and specially prepared drying oils. These oils were produced at the University of Minnesota and included many oils which are not found in nature.

The oils that were prepared and sent to many co-operating institutions, both in this country and abroad were

1. Dehydrated Castor Oil
2. Pentaerythritol Tetralinoleate
3. Glyceryl Trilinoleate
4. Glyceryl Trilinolenate
5. Pentaerythritol Oleate
6. Dipentaerythritol Linoleate
7. Dipentaerythritol Oleate
8. Pentaerythritol Linolenate
9. Dipentaerythritol Linolenate
10. Oleic Acid Pentaerythritol Long Oil Alkyd
11. Linoleic Acid Pentaerythritol Long Oil Alkyd
12. Linolenic Acid Pentaerythritol Long Oil Alkyd
13. Trieleosterin
14. Trilinolenin
15. Eleostearic Glycerol Short Oil Alkyd
16. Linolenic Glycerol Short Oil Alkyd
17. Oleic Pentaerythritol Short Oil Alkyd
18. Linolenic Glycerol Long Oil Alkyd
19. Linoleic Glycerol Long Oil Alkyd
20. Linoleic Glycerol Short Oil Alkyd
21. Pentaerythritol Eleostearate
22. Eleostearic Glycerol Long Oil Alkyd
23. Commercial Alkyd
24. Varnish Linseed Oil

Cooperating in this overall research program, the University of Louisville was assigned the problem of determining the rate of oxidation, the solvent solubility, and the fatty acid adsorption of films prepared from the twenty-four synthetic oils.

This thesis is a continuation of the work initiated by M.M. Moudgill (2), using the methods of semi-micro combustion and solvent extraction developed by him. Together with these, a fatty acid adsorption method was developed.

HISTORICAL

The Chinese were probably among the first to use drying oils although the Egyptians were known to have used drying oils in their process of mummification. No record has been found, however, which indicated that the Egyptians used the oils for any other purpose. Even during Greek and Roman times, resins and oils were used for therapeutic purposes only, and none of the writings of the age make any mention of their incorporation in varnishes or protective coatings.

To Galen (3), in the second century, is attributed the honor of being the first person to record the use of driers and drying oils, while Jacobus de Tholeto, in 1440, is reported as the first to formulate a varnish (4).

It is noted that protective coatings were used in the Orient as early as the seventh century (5), with the mediums used including shellac, sealing wax, gum arabic and tree sap. The Japanese are said to have placed a tax upon the sap of the varnish tree, which was used in waterproofing drinking vessels and for coating armor and leather.

Even in this country, the early American Indians have been found to have used salmon eggs, both fresh and dried, for vehicles prepared by chewing the eggs with the bark of red cedar (5). Many of their earthenware utensils, and handmade artifacts, still retain some of their original art work by virtue of the vehicles used in the manufacture of the decorative coatings.

It was not until the Renaissance, and after however, that very great interest was shown in oils. Linseed oil rapidly came into use in preparing rosin, amber, and sandarac varnishes; and an ever increasing need was felt by the world of art for the development or discovery of new vehicles for paint pigments. Leonardo Da Vinci and Michaelangelo were among the first to experiment with and develop new methods of producing paints and protective coatings for their canvases and murals. Indeed, it was during this period of development that the use of driers in paint and varnishes were first mentioned as having a practical value.

It was not until 1773 that the paint and varnish industry, as we know it today, was described by Watkins, and his book on varnish formulae was considered a standard text for varnish makers until about 1900. It is remarkable to note that in the period from 1776 to 1900 the book was re-printed fourteen times.

With the advent of the industrial revolution and its entailing stimulus to the scientific approach and method, the paint and varnish industry began to advance rapidly. More products were developed and new uses found for old products. It became an increasingly more important factor in the economic life of the nation. The drying oils began to be examined both chemically and physically with the view of determining the reasons behind the phenomena of the drying process. Nonetheless, it was not until about two or

three decades ago that the present theories began to be developed. Several papers were published dealing with oxidation and the mechanism of film formation of the drying oils (6,7,8,9,10). In 1929 and 1930, Carothers (11) and Kienle (12) developed the idea of functionality to clarify the working principles of polycondensation reactions in resins, and Bradley (13) later extended the concept to the reactions of oil-drying.

With the rapid increase in knowledge during the past twenty years, methods have become available, that have allowed the various components of the drying oils to be separated or synthesized, and much work is being done on the esterification of fatty acids, both with glycerol and the higher alcohols (14,15,16,17), as well as on the preparation of drying oils, or drying oil substitutes, from petroleum (18,19,20).

It has been only within the past ten years that pentaerythritol, which was first made commercially in Germany during the first World War and later in Italy during the Ethiopian campaign, has become important in the U.S. market. Its original use in Germany, Italy, and the United States was as a raw material in the preparation of explosives, but its unusual properties when reacted with fatty acids soon became recognized, and its use was extended into the field of drying oils.

Pentaerythritol has been recognized since the time it was first synthesized by Tollens in 1891, and its unique properties have caused it to be studied so extensively that today a great deal of fundamental knowledge concerning it has been assembled. Since it does not occur in nature, but is wholly synthetic, its use in the manufacture of the esters of fatty acids opens up a new field of pure synthetic drying oils, which in time may replace the oils obtained from agricultural materials.

It is with this work as a foundation that the Federation undertook to build a structure of fundamental knowledge concerning the true physical and chemical nature of the reactions of the drying oils.

THEORETICAL

Drying oils are a subdivision of a large class of semi-viscous, non-volatile liquids, which are of either animal, vegetable, mineral, or synthetic origin. They are distinguished from the closely related non-drying and semi-drying oils by a high degree of unsaturation and a correspondingly high iodine value, which, numerically, is above 135. They are unsaturated fatty acid esters existing in nature almost exclusively as glycerides of the C_{12} , C_{14} , C_{16} , C_{18} , C_{20} , and C_{22} acids.

More recently, drying oils have been synthesized from the fatty acid esters of mannitol, sorbitol, pentaerythritol, and dipentaerythritol (17, 21, 22).

Their name refers not to the idea that they lose moisture by evaporation, but rather to the fact that they possess the ability of transforming from a liquid oil to a solid non-tacky surface when coated out in a thin film and exposed to the air. Their drying is a chemical process, and it is generally agreed that two stages are involved:

1. oxidation at unsaturated carbon bonds,
2. polymerization and molecular aggregation of the oxidation products.

Much has been said and written concerning these reactions and the mechanisms by which they participate in the drying process, but very little definite evidence has been presented on the exact course that they follow.

OXIDATION

The stages in the oxidation of drying oils by air has been broken down by Powers (23) into inhibition, peroxide formation, peroxide decomposition, and polymerization. Fig. 1 (23) illustrates the behavior of the changes encountered at each stage of the oxidation. The scale is arbitrary and may vary greatly with the conditions and materials used. In the inhibition step the end of the phase is quite apparent and, at early stages of the oxidation, peroxides are the only products formed. Beyond this point, phase separation of the various steps is purely artificial. Peroxidation does not necessarily cease when rearrangement begins, and polymerization may well begin with the decomposition of the peroxides.

The induction period ends when oxygen absorption begins, and the peroxidation step may be considered to continue to the maximum peroxide value. Peroxides then largely disappear although oxygen may continue to add to the oil. It has been found that synthetic unsaturated esters do not show an induction period (24). Contrary to Powers (23), it has been noted in this work that polymerization continues long after the oil has apparently absorbed the maximum amount of oxygen. However, this may be due to the fact that oxidation, if it does continue longer than polymerization, is so slow that it would take an appreciable length of time for the oil to absorb a detectable amount.

Fig. 1 OXIDATION STAGES OF DRYING OILS (23)

It is generally agreed that oxygen first adds to drying oils by forming peroxides, but their structure and position in the oil molecule are not yet entirely clear. Until recently, the addition of a molecule of oxygen to the double bond has been generally accepted to produce a cyclic peroxide:

Farmer (25), however, considers the structure so sterically unstable that it is probable that its occurrence is only momentary.

Paquet (25) has proposed an ethylene dioxide structure, that should exhibit the same properties as the four membered ring peroxide:

Such a structure is suggested by the high content of esters (26,27) found in oxidized oils and unsaturated acids, as

does the isolation (27) of dihydroxystearic acid by hydrolysis.

Farmer (25), on the other hand, is of the opinion that initial oxygen addition is at the double bond, forming a biradical:

This combines with another unsaturated group, yielding two radicals:

These continue the chain reaction forming α -methylene hydroperoxides. Bolland and Koch (28) have shown that a preliminary oxidation product at room temperature is a mono-hydroperoxide that is conjugated to at least 70%.

During the early stages of oxidation, the peroxide value accounts for nearly all the oxygen added, but the action of temperature, light, driers, acids, and bases accelerate peroxide decomposition, and other oxygen compounds

are found as the decomposition products.

Four decomposition reactions have been indicated and are as follows:

(Dehydration)

(Reduction)

(Rearrangement)

(Rupture)

These reactions are expressed in terms of the cyclic peroxide structure which generally has been used to explain the products formed. Evidence supporting the mechanisms of dehydration and reduction have been presented, but little if any has been set forth in favor of the rearrangement or rupture type of reactions.

Long (30) has suggested that the peroxide structures go through the following reactions giving an essentially metastable state of equilibrium between the peroxide, a ketol, and an unstable diol:

The more recent evidence seems to favor this type of equilibrium although the exact products participating in the above mechanism have not been made definitely clear.

The semi-micro combustion technique previously developed for this work (2) was used to determine the oxygen

content of the synthetic oil films at various time intervals. With this figure an index of the degree of oxidation could be obtained, and the effect of the structures of the various oils studied in relation to their rate of oxidation. It can be seen from the reactions proposed by Long (30) that once complete oxidation has been attained no further change in molecular ratio should occur.

POLYMERIZATION

With the beginning of peroxide decomposition and possibly even before, the oil molecules initiate a state of growth which is accompanied by a rapid increase in density, a rapid decrease in specific refraction, and a rapid drop in iodine value. This molecular growth is characterized by the formation of three dimensional polymers from essentially linear molecular chains.

Carothers (11), in 1929, observed that polymerizations are but the ordinary reactions of organic chemistry, and that they proceed in multiple fashion because of the multiplicity of reactive groups present in the structure of the polymerizing material. In addition, he established the concept of the degree of "functionality", which deals with the effective number of bonds or points of intermolecular attachment present in a polymerizable molecule. This concept establishes whether an oil system produces an essentially

linear or two-dimensional polymer or a cross-linked or three-dimensional polymer. Bradley (13) points out that it is generally considered that all fusible and/or soluble polymers are basically of the linear form, while infusible and insoluble polymers are of the cross-linked or three-dimensional type.

In the polymerization of drying oil at room temperature, oxygen or an oxygen containing compound catalyzes the reactions since similar ones occur at a much higher temperature in vacuum. Peroxide formation and decomposition, plus molecular rearrangement, with the attendant increase in diene conjugation, have much to do with the manner in which the molecules tend to polymerize.

Elm (31) has observed that certain physical and chemical properties of the drying oils during and after drying, such as rapidly increasing viscosity, the swelling of films when exposed to organic liquids and so forth, prove that the originally non-colloidal oils are transformed into colloidal systems when exposed to oxygen. From these facts, he has concluded that oxidation alone cannot be responsible for the formation of a colloidal system, and polymerization of the esters must be assumed in the formation of three-dimensional, cross-linked polymers.

Two types of polymerization reactions might take place: (1) the combination of unsaturated compounds by primary chemical linkages to form larger molecules of a less

saturated or unsaturated type -- true polymerization; or
 2) combination of the same types of compounds by means of
 secondary or residual valencies to form large molecules -
 association.

Direct polymerization of the C-C linkages would
 result in the formation of carbon atom rings which have
 never been detected in oil films, while polymerization
 through the combined oxygen appears more likely. Marcusson
 (32) and Treibs (33, 34) postulate that a dioxane link joins
 the fatty acid segments and that this ring can be assumed
 to be formed by the rearrangement or decomposition of a per-
 dioxane ring:

However, the presence of the dioxane ring has never been
 established, and the reason has never been explained why the
 mechanism does not operate in the case of oleic acid esters
 which show a negligible tendency to polymerize under normal
 conditions.

Association type reactions may be illustrated as follows:

Latest evidence seems to favor this type of reaction over that of the primary chemical linkage type. Products formed by an association of secondary valences and a polymerized molecule held together by primary valence should act differently when treated with solvents, in as much as true polymerides should be affected by chemical reagents only. Elm (31) was able to separate films into different phases by the use of various types of solvents. He found that carbon tetrachloride dissolves the lower, benzene the medium, and acetone the higher associated products while the strongest type are soluble in acetone when treated at 100° C in a closed tube. In this way the film can be completely depolymerized by solvent action, which would hardly be true if the molecules were bonded together by primary valence forces.

With this method, insolubility figures may be obtained, and it is possible to determine the extent to which

an oil has polymerized beyond a certain molecular weight, which in turn is dependent upon the solvent power of the solvent. No quantitative figures are available, however, on the molecular weights that determine the limits between soluble and insoluble polymers for each individual solvent, and extraction results, therefore, are comparative rather than absolute indices of the extent of polymerization.

To summarize - drying process can be assumed to take three steps:

- 1) oxidation of the unsaturated compounds to some type of peroxide structure which will follow the association type reaction,
- 2) polymerization of these associable compounds,
- 3) rearrangement and gelation of the colloidal system formed thereby.

ADSORPTION

Very little work has been done on the adsorption of fatty acids by drying oil films. Long, Zimmerman, and Nevin (35), however, have shown that the number of grams of oleic acid adsorbed per gram of linseed oil film remained essentially constant over the entire drying time, when the percentage of extractable liquid decreased with a corresponding increase in solid phase. These results seemed incompatible. For if the liquid was held mechanically entrained by the ever

growing complexity of the gel structure, the percentage of it taken up would decrease as the solid network increased from week to week. If the adsorption was dependent on the intricacy of gel texture, however, it should increase with time.

This dilemma was resolved by assuming that the adsorbed liquid is definitely oriented in the solid gel phase. The theory is entirely compatible with that of Langmuir (36), which pictures adsorption as related to the chemical constitution of the substances concerned.

Hence, by allowing different types of drying oil films to adsorb the same fatty acid, results should be obtained which may aid in clarifying the picture of the chemical structure of the drying oil films.

EXPERIMENTAL

The experimental procedures used in this work were those developed by M.M. Moudgill (2), with the exception of the procedure for oil adsorption. The procedures included, essentially, the following steps:

I. Film Formation, covering:

- a) Mixing
- b) Brushing
- c) Scraping

II. Combustion

III. Extraction

IV. Oleic Acid Adsorption

Linseed oil films were analyzed to gain proficiency in working with the various experimental techniques. Certain minor modifications were applied to the combustion apparatus, while a new technique, that of brushing, was used in film formation.

The synthetic materials analyzed are listed in the order in which they were examined and are as follows:

- A. Glyceryl Trilinoleate
- B. Pentaerythritol Tetralinoleate
- C. Pentaerythritol Oleate
- D. Pentaerythritol Oleic Acid Long Oil Alkyd
- E. Dipentaerythritol Linoleate
- F. Dipentaerythritol Linolenate
- G. Pentaerythritol Linolenate

No difficulties were encountered, but certain properties of some of the oils were noted. Some of the oils were seen to exhibit a tendency to crawl. This has also been mentioned in a personal communication from L.G. Montague to Dr. J.S. Long (36). The oils noticed to exhibit this tendency were 1) Pentaerythritol Tetralinoleate (to a slight extent); 2) Pentaerythritol Oleate (very marked); 3) Pentaerythritol Oleic Acid Long Oil Alkyd (very marked); 4) Dipentaerythritol Linolenate (slight). No shrinkage or crawling was noticed with the other materials tried.

FILM FORMATION

a) Mixing

Following the previously adopted method, 0.015% by weight of cobalt naphthenate or 0.5% by weight of lead naphthenate were added to the drying oils. The oil samples were mixed in a small 25 ml. pyrex Florence flask, using a hypodermic needle and syringe. This was done to avoid sample wastage since samples of 3 gram or 5 gram quantities were used. The drier was introduced into the mixing flask (usually 4 or 5 drops), weighed, and the desired quantity of oil added, as calculated from the weight of drier (Table XV) to give the required percentage of drier in the mixture. This method of mixing was used until the drier, formulated especially for the Federation by the Nuodex Corporation,

became available. The drier was so made up that 1 ml. contained 2.5 mg. of Cobalt metal and 3.0 mgs. of Lead metal. Each 0.1 ml. per gm. of oil gave 0.025% Cobalt and 0.03% Lead in the mixture. This drier was used for the Dipentaerythritol Linolenate and Pentaerythritol Linolenate samples. A 1 ml. syringe graduated in 0.1 ml divisions was used to introduce the drier into the mixing flask. For a three gram sample of oil 0.3 ml. of drier was added, and for a five gram sample 0.5 ml. of drier was added. The oil samples were then introduced into the mixing flask and the flask then placed under vacuum; after which the mixture was allowed to stand for 48 hours before it was used for film formation.

b) Brushing

The glass plates, upon which the oil films were spread, were prepared from photographic plates formerly employed in micro-metallographic analyses. The plates were first soaked in hot water, and when the emulsion had become soft enough, it was scraped off with a razor blade and the plates were washed with soap and water until an even water film was seen to remain on the surface. The plates were then placed in a sulphuric acid, potassium dichromate cleaning solution and allowed to remain there completely immersed for twenty-four hours before they were used. After the oil had been mixed and was ready to be spread upon the glass surface, the plates were removed from the cleaning solution,

washed with water, and wiped with a piece of cotton soaked in acetone. (A final wiping with clean dry cotton cleared away any wet marks left by the evaporating acetone). The plate was weighed using a keyboard chainomatic balance (2), and the weight recorded. Knowing this weight, the area that the film was to cover (this can vary with the size of plate used), the film thickness wanted, and assuming a Sp. Gr. for the oils of 0.95, the weight of oil to be brushed upon the plate was calculated. It was found to be 0.1685 gm. per normal plate for a thickness of 1.25 mil. This figure for film thickness was used since it was felt that it would allow for variation in film thickness of from 1.0 to 1.5 mils, which is within the limits required.

Knowing the weight of the plate and the weight of the oil to be measured onto it, the weighed plate was then placed upon a second plate, which had the area in which the oil was to be coated marked off with a marking crayon. The oil was then brushed out upon the plate with a small artist's camel's hair brush (which had been washed previously in acetone and air dried), and the plate reweighed. This was repeated until the required weight of oil was attained. The plate was then marked on the under side, using a marking crayon, with the name of the oil and the date, and then placed under a transparent cover to permit the oil film to air dry.

e) Scraping

The method for removing the dried oil film, was exactly that used in the development of this work. A clean razor blade, mounted in a holder, and inclined at about its cutting edge, was used. A little difficulty was found in removing some of the oil films, and extreme care had to be taken so that the razor blade was not broken or the film chewed up. It was found that after two or three scrapings a new blade had to be used, since the older blade had become dented or dull and the film could not be removed properly.

II. COMBUSTION

The combustion train used for the ultimate analysis of the drying oil films, was arranged in exactly the same manner as described by Moudgill (2). Minor additions were made to it, however, to make operation more efficient, and to eliminate two possible sources of error.

Previously some difficulty was encountered because the rubber stopper used to close the sample end of the combustion tube, and through which passed a glass tube for the oxygen stream, burned when the sample was heated to combustion with a bunsen burner.

This difficulty was solved by wrapping gauze surgical bandage about the combustion tube directly around the stopper. One end of the gauze was allowed to dangle into a large-mouth bottle containing some water while from

an inverted test tube, a regulated stream of water was allowed to flow down over the covering. Regulation of the water flow was achieved by varying the pressure of a screw clamp upon a piece of rubber tubing attached to a long glass tube extending up through a two holed rubber stopper into the inverted, water filled test tube. In this manner the air entering could be controlled, and thus, the water flow. A smaller glass tube extended through the second hole in the stopper to just above the inside surface, and through this the water flowed down upon the gauze surrounding the combustion tube stopper. In this manner the area around the rubber stopper could be kept cool enough to prevent burning while the sample itself could be heated to combustion and higher.

A further addition was a removable coil of copper from which extended a straight piece of wire. This was placed over the inlet arm of the drierite absorption tube. The wire extending from the coil while the absorption tube was attached to the train was heated by a small flame from a bunsen burner. This allowed enough heat to be conducted to the surface of the absorption tube arm to prevent any moisture formed in combustion from condensing and thus not be absorbed by the drierite.

Operating conditions remained the same with combustion time for all samples being 2 hours.

A. Glyceryl Trilinoleate

No difficulty was encountered in the analysis of this material, and the results of combustion analyses through 51 days may be seen in Table I and Fig. 2. Disregarding the free moisture on the film, the maximum theoretical oxygen content should be 26.9%. However, since no moisture corrections were made, a maximum percentage of 29-30% is within tolerance limits. With 3% moisture correction, the curve in Fig. 2 would move to the position as indicated by the dotted line.

Analyses were not carried further since no film remained, but the trend is evident from the curve.

B. Pentaerythritol Tetralinoleate

No appreciable difficulty was encountered with this material, but it was found that extreme care had to be taken to heat the sample slowly. If the sample were heated too rapidly, it exploded, and the rubber stopper closing the combustion tube was blown out. The results of this analysis are shown in Fig. 3 and Table II. These figures and all those following are corrected for 3% free moisture on the film.

C. Pentaerythritol Oleate

Much difficulty was encountered in analyzing this material since it apparently does not dry. Figures were obtained for the first and fifth days after the oil was

brushed out into a film, and they were 13.28% oxygen and 12.44% oxygen respectively. After several unsuccessful attempts to analyze the oil scraped from the glass plate, further analysis was discontinued until such time as the film became tacky. After four months the film is still as liquid as when first laid.

D. Pentaerythritol Oleic Acid Long Oil Alkyd

The same difficulties were encountered with this material as with pentaerythritol oleate. The film remained liquid until about two months after it was laid. After that time it started becoming tacky, and analyses were run on the 64th and 72nd day after the film had been brushed out. The oxygen percentages were found to be 19.9% and 20.95% respectively. After three months, the film is still tacky and difficulty in scraping enough sample from the glass plate has caused several unsuccessful analyses.

E. Dipentaerythritol Linoleate

This material gave no trouble and formed a hard, tack-free film, twenty-four hours after being brushed out on the glass plates. The results may be seen in Fig. 4 and Table III. It should be noted that as time went on, the films became harder and harder and were more difficult to remove with the razor blade.

F. Dipentaerythritol Linolenate

This material acted as expected, and results are shown in Fig. 5 and Table IV. The films became harder and more difficult to remove from the glass plate as they aged.

G. Pentaerythritol Linolenate

No difficulty was encountered with this material, and results are shown in Fig. 6 and Table V. The films became harder with increasing age.

For comparison purposes, Fig. 7 and Table VI show results obtained from Linseed oil films, and Fig. 8 and Table VII those for Soybean oil.

It was found that the drierite absorption tube had to be repacked every week, since at the end of a week's time it had become sufficiently saturated that some of the water of combustion was being absorbed by the ascarite rather than the drierite.

In order to determine the amount of free moisture adsorbed from the air upon the surface of the films, the films were weighed before and after a two hour desiccation over phosphorous pentoxide. The results of these determinations showed an average of about 3% free moisture upon the film surfaces, and this figure was used in correcting the combustion results.

Analyses will be continued on all the samples through 365 days after initial brushing and some films of

all the materials will be placed aside to age for about five years.

TABLE I. COMBUSTION OF GLYCERYL TRILINOLEATE

Film Age in Days	1	2	4	7	14	51
% C	61.5	57.7	59.0	61.0	61.8	56.5
% H	11.6	10.7	10.1	10.0	9.3	9.3
% O	26.7	31.6	30.9	29.0	28.9	34.2

This series of combustions was conducted using a silica combustion tube at 650°C, 0.5% (wt. % Pb.) lead naphthenate, and a two hour combustion period. Oxygen percentage were calculated by difference. (See appendix, Table 15)

Corrected figures for 3% free moisture on film

Film Age in Days	1	2	4	7	14	51
% C	63.4	59.4	60.8	62.9	63.1	58.4
% H	11.8	10.6	10.0	10.0	9.3	9.3
% O	24.8	30.0	29.2	27.1	26.8	32.3

O-Experimentally Determined
 X-Corrected for 3% Free
 Moisture (Table I)

FIG. 2 RATE OF OXIDATION OF GLYCEROL TRIOLLEATE

TABLE II. COMBUSTION ANALYSIS OF PENTAERYTHRITOL
TETRALINOLEATE

Film Age in Days

	1	2	3	4	5	7	14
% C	73.50	68.00	67.50	67.00	67.30	65.40	65.80
% H	9.63	9.00	9.04	9.18	9.04	8.82	9.63
% O	16.87	23.00	23.46	23.82	23.66	25.78	24.57

% C	78.25					63.70	66.20
% H	10.55					10.00	8.40
% O	11.25					26.30	25.40

% C 72.30

% H 12.20

% C 15.50

Film Age in Days

	28	31	48	112
% C	64.20	65.30	63.30	64.60
% H	9.38	9.00	8.86	8.38
% O	26.42	25.70	27.84	27.02

This series of combustions was conducted using a silica combustion tube at 6500C., 0.5% (wt. % Pb.) lead naphenate, and a two hour combustion period. These figures are corrected for 3% free moisture on the film. Oxygen percentages were calculated by difference (Appendix, Table 15).

Fig. 3 RATE OF OXIDATION OF PENTAERYTHRITOL TETRALINOLEATE

TABLE III. COMBUSTION ANALYSIS OF DIPENTAERYTHRITOL
LINOLEATE

Film Age in Days	1	2	4	9	21	58	63
% C	66.10	70.00	67.80	65.50	65.30	62.80	64.00
% H	9.65	10.31	9.34	9.13	9.42	9.76	9.98
% O	24.25	19.69	22.86	25.37	25.28	27.44	26.02

This series of combustions was conducted using a silica combustion tube at 650°C., 0.5% (wt. % Pb.) lead naphthenate drier, and a two hour combustion period. These figures are corrected for 3% free moisture on the film. Oxygen percentages were calculated by difference (Appendix Table 15)

FIG. 4 RATE OF OXIDATION OF DIPENTAERYTHRITOL LINOLEATE

TABLE IV. COMBUSTION ANALYSIS OF DIPENTAERYTHRITOL
LINOLENATE

Film Age in Days	1	2	4	7	23
% C	68.90	70.00	70.00	64.00	63.80
% H	10.05	10.35	10.65	9.35	8.98
% O	21.05	19.65	19.35	26.65	27.22
% C	68.80	65.00			
% H	10.05	9.34			
% O	21.15	25.66			
% C		67.00			
% H		9.35			
% O		23.65			

This series of combustions was conducted using a silica combustion tube at 650°C., 0.3 ml. of Federation drier containing 0.025% Cobalt and 0.03% Lead, and a two hour combustion period. These figures are corrected for 3% free moisture of the film. Oxygen percentages were calculated by difference (Appendix, Table 15)

Fig. 5 RATE OF OXIDATION OF DIPENTAERYTHRITOL LINOLENATE

TABLE V. COMBUSTION ANALYSIS OF PENTAERYTHRITOL
LINOLENATE

Film Age in Days	1	2	3	4
% C	64.00	64.60	65.00	65.80
% H	9.50	9.38	9.08	9.40
% O	26.50	26.02	25.92	24.80
Film Age in Days	7	15	21	32
% C	65.50	66.80	62.80	65.50
% H	9.85	9.88	9.33	6.83
% O	24.65	23.32	27.87	27.67

This series of combustions was conducted using a silica combustion tube at 650°C., 0.3 ml. of Federation drier containing 0.025% Cobalt and 0.03% Lead, and a two hour combustion period. These figures are corrected for 3% free moisture on the film. Oxygen percentages were calculated by difference (Appendix, Table 15)

Fig. 6 RATE OF OXIDATION OF PENTAERYTHRITOL LINOLENATE

TABLE VI. COMBUSTION ANALYSIS OF LINSEED OIL

Film Age in Days	1	2	3	4	7	9	12	14
% C	61.88	58.93	59.48	59.29	55.70	56.70	59.84	61.59
% H	11.19	10.35	9.83	9.93	11.75	9.19	12.44	9.44
% O	26.93	30.72	30.69	30.78	32.55	34.11	28.67	28.97
% C	59.48	59.78	This series of combustions was conducted using a silica combustion tube at 650°C., and 0.1% (wt.% Pb.) lead naphthenate drier. Oxygen percentages were calculated by difference. (Appendix, Table 15)					
% H	12.91	10.01						
% O	27.61	30.21						
% C	63.83							
% H	11.78							
% O	24.39

FIG 7 RATE OF OXIDATION OF LINSEED OIL

TABLE VII. COMBUSTION ANALYSIS OF SOYBEAN OIL

Film Age in Days	1	2	3	4	7
% C	57.70	53.50	58.40	54.50	54.00
% H	7.32	7.40	6.30	9.40	8.50
% O	34.98	39.10	35.30	36.10	37.50

This series of combustions was conducted using a silica combustion tube at 650°C., and 0.1% (wt. % Co.) Cobalt naphthenate drier. Oxygen percentages were calculated by difference. (Appendix, Table 15)

FIG. 8 RATE OF OXIDATION OF SOYBEAN OIL

III EXTRACTION

The extraction apparatus as used by Moudgill (2) was employed without modification and the solvent, carbon tetrachloride, that he found most suitable, gave no difficulty. Only one modification was made in the operating procedure. Instead of drying the extracted materials in an oven at 94°C , they were placed in a constant temperature, vacuum unit to dry, thus eliminating the danger that the films might be burned if the oven went above the required temperature. The unit used consisted of two vacuum filter flasks which were attached to a common vacuum line. These flasks were then immersed in water which was kept boiling (100°C) by an electric heater. The samples were placed in wire cradles suspended from the rubber stoppers that closed the flasks. About one hour was sufficient to dry the samples.

A. Glyceryl Trilinoleate

Results are shown in Table VIII and Fig. 9. No unusual results were noted except that the film became highly discolored on extraction, but still remained pliable.

B. Pentaerythritol Tetralinoleate

Results are shown in Table IX and Fig. 10. Here again the film was discolored and slightly brittle.

C. and D. Pentaerythritol Oleate and Pentaerythritol Oleic Acid Long Oil Alkyd

No extractions were run on these two materials since

they were still liquid or slightly tacky and hence had not begun to polymerize.

E. Dipentaerythritol Linolenate

Results are given in Table X and Fig. 11. With this material also, discoloration of the extracted film was evident and the film was brittle.

F. Dipentaerythritol Linolenate

Results for this material are shown in Table XI and Fig. 12. It is with this material that an unusual phenomenon was noted. On extraction with carbon tetrachloride, it was noticed that the film became very brittle as well as highly discolored. In addition the film seemed to have deteriorated appreciably leaving a needle-like or fibrous structure. It was seen, that on the first day of extraction the film fell apart into these fibers and they were interlaced like a bunch of straw. In addition the fibers were very brittle. This phenomenon was not observed in any of the other materials.

G. Pentaerythritol Linolenate

Results for this material are given in Table XII and Fig. 13. It was with this material that a different phenomenon was noted. The film when extracted, instead of becoming discolored to a brown, as were the others, was changed from a clear, transparent film to a soft, extremely pliable, milky white film.

For comparison purposes, results on the extraction of linseed oil films are given in Table XIII and Fig. 14.

TABLE VIII. EXTRACTION OF GLYCERYL TRILINOLEATE FILM
WITH CARBON TETRACHLORIDE

RUN NO.	Film Age in Days	Insoluble Original	Percentage Duplicate
1	1	41	44
2	2	49	48
3	4	51	50
4	7	59	56
5	14	54	58
6	28	61	63

(See Appendix, Table 16)

FIG. 9 EXTRACTION OF GLYCERYL TRILINOLEATE WITH CARBON TETRACHLORIDE

TABLE IX. EXTRACTION OF PENTAERYTHRITOL TETRALINOLEATE
WITH CARBON TETRACHLORIDE

RUN NO.	Film Age in Days	Insoluble Original	Percentage Duplicate	Additional
1	1	49.3	36.0	
2	2	52.0	48.8	42.4, 46.6
3	4	74.3	69.6	67.6
4	7	70.6	69.5	
5	8	73.3	74.8	
6	14	77.3	---	
7	15	77.8	74.8	
8	113	82.3	85.8	

(See Appendix, Table 16)

FIG 10 EXTRACTION OF PENTAERYTHRITOL TETRALINOLEATE WITH CARBON TETRACHLORIDE

TABLE X. EXTRACTION OF DIPENTAERYTHRITOL LINOLEATE FILM
WITH CARBON TETRACHLORIDE

RUN NO.	Film Age in Days	Insoluble Original	Percentage Duplicate
1	2	80.0	76.4
2	4	75.3	99.6
3	9	82.3	65.4
4	22	72.3	69.3
5	56	77.8	76.1
6	63	78.4	69.7

(See Appendix, Table 16)

FIG 11 EXTRACTION OF DIPENTAERYTHRITOL LINOLATE WITH CARBON TETRACHLORIDE

TABLE XI. EXTRACTION OF DIPENTAERYTHRITOL LINOLENATE FILM
WITH CARBON TETRACHLORIDE

RUN NO.	Film Age in Days	Insoluble Original	Percentage Duplicate
1	1	77.7	78.6
2	2	83.0	83.8
3	4	93.8	91.0
4	6	82.8	80.8
5	7	100.0	97.4

(See Appendix, Table 16)

Fig. 12 EXTRACTION OF DIPENTAERYTHRITOL LINOLENATE WITH CARBON TETRACHLORIDE

TABLE XII. EXTRACTION OF PENTAERYTHRITOL LINOLENATE FILM
WITH CARBON TETRACHLORIDE

RUN NO.	Film Age in Days	Insoluble Original	Percentage Duplicate
1	2	88.8	81.0
2	3	97.3	98.3
3	7	77.0	69.0
4	14	95.8	96.6
5	40	93.8	90.9

(See Appendix, Table 16)

FIG. 13 EXTRACTION OF PENTAERYTHRITOL LINOLENATE WITH CARBON TETRACHLORIDE

TABLE XIII. EXTRACTION OF LINSEED OIL FILM WITH
CARBON TETRACHLORIDE

Run No.	Film Age in Days	Insoluble Original	Percentage Duplicate	Additional
1	1	27	16	--
2	2	21	18	--
3	3	--	26	--
4	4	30	28	--
5	5	35	32	--
6	6	41	29	38
7	7	44	30	40
8	11	47	43	--
9	12	35	44	--
10	20	48	45	--
11	26	47	37	--
12	31	50	44	--

(See Appendix, Table 16)

FIG. 14 EXTRACTION OF LINSEED OIL WITH CARBON TETRACHLORIDE

IV. ADSORPTION

The adsorption experiments were begun with the Dipentaerythritol Linoleate extraction. After the films were extracted, dried, and weighed they were placed in a 25 ml. test tube and 10 ml. of Oleic Acid added. The test tube was then closed with a rubber stopper through which projected a glass tube. Attached to the tube was a small piece of rubber tubing which could be closed off by a screw clamp. After the test tube was closed the rubber tubing was attached to an aspirator and a vacuum drawn. Bubbles could be seen rising from the film soaking in the oleic acid, as the occluded air was displaced by the liquid. After the vacuum had been drawn the rubber tubing was clamped tight, and the test tube placed away for twenty-four hours. At the end of that time the test tube was opened, the oleic acid decanted, and the soaked film placed on a filter paper. The film was then pressed in the filter paper until no further liquid could be extruded, and then placed in its original extraction thimble and reweighed. Its gain in weight is the weight of oleic acid adsorbed.

It was found that the weight of oleic acid adsorbed to the weight of the extracted film was nearly a 1.5 to 1 ratio. Table XIV indicates some of the results.

TABLE XIV. ADSORPTION OF OLEIC ACID BY EXTRACTED
DRYING OIL FILMS

Film Material	Film Age in Days							
	1	2	4	7	22	40	56	63
Dipentaerythritol Linoleate	-	-	-	-	1.32	-	1.23	1.30
Dipentaerythritol Linolenate	1.59	1.01	1.16	-	-	-	-	-
Pentaerythritol Linolenate	-	1.51	-	1.25	-	-	1.31	-

The figures above are the ratio of gms. of oleic
acid adsorbed to gms. of extracted film.

CONCLUSIONS

From the results thus far obtained in combustion and extraction of the drying oil films, it would seem that the theory of Carothers (11) and Bradley (13) are more nearly substantiated. As was previously pointed out by them, the reaction involved in the drying process are essentially those of ordinary organic chemistry, and the rate at which an oil dries is dependent upon the structure and functionality of the molecules involved.

From the curves of the individual materials it can be seen that those materials having a great many functional groups absorb oxygen and polymerize faster than do materials having less functional groups. Moreover, the esters of the poly-alcohols dry more rapidly and polymerize even more rapidly than do the esters of glycerol. This is shown to be true by the almost complete polymerization of the dipentaerythritol esters in seven days time while the glycerol ester had only attained 54% solid material in the same length of time.

Also the oxidation and polymerization reactions are simultaneous and quite rapid, during the first few days, and after the oil film has absorbed essentially the maximum amount of oxygen, polymerization reduces to a gradual rate.

Comparing the synthetic esters to linseed oil their rate of oxidation is about the same with the exception of the dipentaerythritols. This can be explained by remembering that the number of unsaturation points is about the same

since linseed oil contains glycerides of both linoleic and linolenic acids. The dipentaerythritols probably dry faster than linseed oil because the number of unsaturation points is greater. The fact that pentaerythritol oleate does not dry at all is an excellent indication that number of unsaturation points has a great deal to do with the rate of which a particular oil will dry.

The assumption that polymerized materials are aggregates of like molecules held together by secondary forces is very nicely illustrated in the extraction of dipentaerythritol linolenate. The fact that the oil film disintegrated under the action of the solvent, although it was almost 80% solids, would indicate that secondary rather than primary forces were involved.

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APPENDIX

TABLE XV SAMPLE CALCULATIONS FOR MIXING DRIER AND OIL

Drier used	--- Lead Naphthenate
Wt. % Pb in drier supplied	= 24 %
Wt. % Pb in mixture (specified)	= 0.5 %
Approximate weight of mixture	= 2 gms.
Approximate weight of drier	= $\frac{0.5}{100} \times \frac{100}{24} \times 2$ gms.
	= 0.04 gms.
Let	
Wt. of Florence flask empty	= 17.2473 gms.
Wt. of Florence flask and drier	= <u>17.2884</u> gms.
Wt. of Drier used	= 0.0411 gms.
Corresponding weight of mixture	= $0.0411 \times \frac{24}{100} \times \frac{100}{0.5}$ gms.
	= 1.973 gms.
Wt. of Oil to be added	= 1.973 - 0.0411 gms.
	= 1.9319 gms.
Wt. of Florence flask, drier & oil	= 19.2203 gms.

This method was used prior to the arrival of the drier especially prepared for the Federation by the Nuodex Corporation.

TABLE XVI SAMPLE DATE SHEET

Combustion of

Film Age in Days	1.	2.	3.	7.	14.
------------------	----	----	----	----	-----

(1) Wt. sample and combustion tube

(2) Wt. combustion tube

(3) Wt. of sample (1) - (2)

(4) Initial wt. Drierite tube

(5) Final wt. Drierite tube

(6) Wt. of H₂O formed (5) - (4)

(7) Initial wt. Ascarite tube

(8) Final wt. Ascarite tube

(9) Wt. of CO₂ formed (8) - (7)

$$(10) \%C \quad \frac{(9)}{(3)} \times \frac{12}{44} \times 100$$

$$(11) \%H \quad \frac{(6)}{(3)} \times \frac{2}{18} \times 100$$

$$(12) \%O \quad 100 - (10) - (11)$$

TABLE XVII SAMPLE DATA

Extraction of

Film Age in Days	1.	2.	3.	7.	14.
------------------	----	----	----	----	-----

(1) Wt. filter-paper and thimble

(2) Wt. sample, " " initial

(3) Wt. sample, " " final

(4) Wt. of unextracted film (2) - (1)

(5) Wt. insoluble portion (3) - (1)

(6) Wt. % Insolubility $\frac{(5)}{(4)} \times 100$.

Solvent

B. Pt.

Approx. Solvent Loss (Vol. %)

VITA

The author was born in Boston, Massachusetts, on August 9, 1925. His father, Mr. Philip Cooperman, and mother, Mrs. Anna Cooperman (née Anna Krasnitzsky), were both born in Russia.

His primary education was initiated at the Prescott school in 1931, and in 1937 he entered the Boston Latin School whence he graduated in June of 1943, after completing the six year course. In July of the same year he entered Northeastern University in Boston, where, after two years and eleven months under the war-time accelerated program, he received his B.S. degree in Chemical Engineering in June of 1946.

In June of 1947 he secured a position with Joseph E. Seagram and Sons, distillers, at their Lawrenceburg, Indiana, plant, and there worked in the control laboratory until March of 1948. At that time he was granted a research fellowship by the University of Louisville, Speed Scientific School, and that same month went to work at the Institute of Industrial Research connected with the school. In August of that year he transferred from the Research Institute to the Department of Chemical Engineering of the Speed School, where he continued to work on the projects sponsored by the National Federation of Oil, Paint and Varnish Clubs. In June of 1949, he completed his work and received the degree of Master in Chemical Engineering.