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UNIVERSITY OF LOUISVILLE

A STUDY OF OLEORESINOUS FILM STRUCTURE

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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

By

Frank Rush McQuilkin

"

1940

A STUDY OF OLEORESINOUS FILM STRUCTURE

Frank Rush McQuilkin

Approved by Examining Committee:

Director

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July 25, 1940

TABLE OF CONTENTS

	Page
List of Tables	ii
List of Figures	iii
Acknowledgement	v
Abstract	vi
Introduction	1
Historical	4
Theoretical	8
Raw Materials	16
Experimental Apparatus	22
Experimental Procedure	33
Data and Results	38
Discussion of Results	57
Conclusions	70
Literature Cited	72
Appendix	74
Acknowledgements _m	75
Vita	76

LIST OF TABLES

Table		Page
I	Raw Materials	19
II	Formulations	20
III	Distensibility and Percent Unextractible of Linseed Varnishes	40
IV	Distensibility and Percent Unextractible of Tung Varnishes	41
V	Distensibility and Percent Unextractible of Linseed Enamels	42
VI	Distensibility and Percent Unextractible of Tung Enamels	43
VII	Extraction of Congo Resin	44
VIII	Percent Unextractible of Films at Failure	56

LIST OF FIGURES

Figure		Page
1	Casting film on tin panel with doctor blade	24
2	Accelerated weathering unit	26
3	Outdoor exposure fence	27
4	View showing micrometer, doctor blade, steel template and stripped films	29
5	Tensile tester used in making the distensibility tests.	30
6	Extraction units used in extracting the films	31
7	Percent Unextractible vs Age and Elongation for 33 gal. Linseed Varnish and Enamel :	45
8	Percent Unextractible vs Age and Elongation for 25 gal. Linseed Varnish and Enamel	46
9	Percent Unextractible vs Age and Elongation for 16 gal. Linseed Varnish and Enamel	47
10	Percent Unextractible vs Age for 8 gal. Linseed Varnish and Enamel	48
11	Percent Unextractible vs Age and Elongation for Straight Linseed Oil Films	49
12	Percent Unextractible vs Age and Elongation for 33 gal. Tung Varnish and Enamel	50

LIST OF FIGURES (continued)

Figure		Page
13	Percent Unextractible vs Age and Elongation for 25 gal. Tung Varnish and Enamel	51
14	Percent Unextractible vs Age and Elongation for 16 gal. Tung Varnish and Enamel	52
15	Percent Unextractible vs Age for 8 gal. Tung Varnish and Enamel	53
16	Percent Unextractible vs Age and Elongation for Straight Tung Oil Films	54
17	Percent Unextractible vs Age for Congo Resin Film . . .	55
18	Composite Curves for 33 gal. Linseed Varnish and Enamel	62
19	Composite Curves for 25 gal. Linseed Varnish and Enamel	63
20	Composite Curves for 16 gal. Linseed Varnish and Enamel	64
21	Composite Curves for 8 gal. Linseed Varnish and Enamel	65
22	Composite Curves for 33 gal. Tung Varnish and Enamel .	66
23	Composite Curves for 25 gal. Tung Varnish and Enamel .	67
24	Composite Curves for 16 gal. Tung Varnish and Enamel .	68
25	Composite Curves for 8 gal. Tung Varnish and Enamel . .	69

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ABSTRACT

This investigation is the first in a series whose purpose is to establish a basis for formulating oleoresinous coatings. A study of the polymerization and distensibility effects accompanying aging was correlated with accelerated exposure durability, showing that a film loses its elastic properties when definite exposure failure has set in. The three-dimensional intermolecular theory of oil polymerization is considered in postulating the cause of the film failure.

The degree of polymerization when failure sets in, as determined by solvent extraction, varies within a range due to the differences in oils and the ratios in which they are used with resin.

Although enamels are observed to polymerize more slowly than varnishes, films of the same materials and oil lengths representing each type of coating fail at the same degree of polymerization. Inert pigment is shown to incorporate itself as 'polymer' when considered in this manner. The enamel failure generally occurs earlier because of the high initial insoluble content imparted by the pigment.

Composite curves are developed to show that rate of polymerization curves for varnishes and enamels containing an in-

ABSTRACT (continued)

ert pigment can be predetermined by similar curves for the individual materials used. Such curves are incapable of predicting the expected durability of the coatings.

INTRODUCTION

This investigation is the first in a series whose purpose is to study oleoresinous film structures so as to establish a sound basis for formulating oleoresinous coatings. Such a basis, if developed from a practical point of view, would be of value to the varnish industry in that the expected durability and properties of a coating could be predicted by formula analysis.

The present investigation is a study of the problem from the basic film structure angle. Assuming that film failure is due to some ultimate combination present when failure occurs and designating this combination as the polymer-to-oil ratio, it is proposed to study the change in this ratio in the film through its life until failure occurs.

The determination of polymer-to-oil ratio has been based upon the assumption made by other investigators: That the portion of the film insoluble in acetone can be considered as an index of the 'polymer' content. The term 'polymer' used here refers to those highly polymerized molecules in the film that have so linked themselves by intermolecular forces that they constitute a continuous network of ring enclosed molecules resembling lattice work. This portion of the film is considered insoluble in acetone and filterable. Thus pigments are included in this portion. The oil portion consists of polymerized and unpolymerized molecules which have not linked themselves into the network of 'polymers'. They are considered soluble and unfilterable in this

work. The Soxhlet method of solvent extraction was employed for the removal of the oil portion. Since this portion of the film has elastic-giving properties we may consider it as the plasticizer portion which will be present in a minimum allowable amount when film failure occurs.

HISTORICAL

Blom (1) has done considerable pioneer work in the field of protective coating film structures. In 1929 he made photomicrographs of the cross section of films showing a stratification of the pigment and other constituents. From this study he suggested that enormous intermolecular forces must be present in films.

Elm (9) investigated the changes taking place in films of trilinolenic glyceride during exposure to room conditions. This investigation was undertaken with the hope that a study of a simple unsaturated glyceride might yield information which would prove helpful in explaining the formation and deterioration of the more complex drying oil systems and the effect exerted upon them by pigments. He concluded that compounds less complicated than trilinolenic glyceride required study if the basic reactions involved in drying oil reactions was to be learned.

Long (13,14) likewise experimented with pure trilinoleic and trilinolenic glycerides in connection with his colloidal association studies. He showed that a dried film may be divided into a soluble and insoluble phase by means of solvent extraction. Acetone was proved the most satisfactory solvent.

After analyzing the soluble liquid phase and the insoluble solid phase of linseed oil films, Rose and Bolley (16) spoke of the three components constituting the films as: (a) liquid, (b) adsorbed liquid, and (c) solid. They claim that the relative proportions in which these components are present have a

decided affect on the physical nature of the film. Linolenic glyceride and linseed oil films have been aged and extracted with acetone and it has been found that the solid phase becomes increasingly greater and the liquid phase decreases as age increases. The unpolymerized and unassociated liquid which has not been adsorbed are completely extracted but probably only a part of the liquid which has been adsorbed is extracted. After continued aging the pigmented oils begin to lose traces of pigment due to changes in oil structure. The authors speak of this as a lessening of 'binding' power of the oil.

As a continuation of Elm's original work Overholt and Elm (15) followed the suggestion that less complicated compounds be used. Methyl esters of several unsaturated fatty acids were exposed to ultraviolet light for various periods of aging after which the films were analyzed for unsaturation, conjugation, oxidation, polymerization, and the change in refractive power. The method of study employed in determining the degree of polymerization was the cryoscopic molecular weight method. This determination was checked by a viscosity measurement for determining the degree of polymerization. The authors did not seem satisfied with their results, however, they considered the possibilities of the work taken up in the present series of investigations. 'The values of these data will be found in the fact that they reduce to a common denominator the changes taking place during a standard

exposure in drying oil esters varying in type and degree of unsaturation. When these results are contrasted with similar data obtained with the more complex glycol and glycerol esters, it should be possible to obtain a clearer insight into the mechanism of film formation of drying oils'.

THEORETICAL

Oleoresinous films and their structures cannot be fully appreciated without considering the chemistry of the drying oils and resins.

Linseed oil consists principally of the triglycerides of the unsaturated fatty acids: Linoleic, 40%; linolenic, 40%; and oleic, 10%. They contain two, three, and one double bonds in the order named. Part of the linolenic acid is in the form of isolonic acid. Also about 5% of stearic acid glyceride is present. Tung oil consists of about 75% of the triglyceride of eleostearic acid, about 15% oleic and 5% palmitic acid glycerides.

The drying oils are capable of two types of reaction, double-bond polymerization and oxygen absorption (5). Cutter and Jordon (7) discussed the mechanism of the double bond polymerization. They modified the Diels-Alder reaction (8) to get a six-membered carbon ring serving to link together two acid radicals. Long's studies (14) on oxygen absorption and loss of volatile products on drying concluded that drying is a 'colloidal association process'. Neglecting double bond polymerization entirely, he presents a two stage drying process. In the first stage, oxygen is absorbed forming polar molecules. These liquid polar molecules then associate to give a solid, insoluble phase. This association is supposed to take place slowly over a period of months, whereas the oxygen absorption is apparently complete in a much shorter time. Association is observable to its fullest extent as soon as the

forces which make it possible are effective.

Bradley's (2) extensive studies of film structure are based on the theory that the tri-blycerides are three-dimensional. He extended the general theory of polymerization developed by Carothers (6) and the related theory of alkyd resins developed by Kienle (11) and applied them to 'drying'. He states that the molecules of soluble resins and coating compounds have linear, 2-dimensional structures, while insoluble resins and dried (insoluble) films have the chains cross-linked in 3-dimensional structures. Drying consists fundamentally in the conversion of the 2-dimensional to the 3-dimensional type of structure. The main requirement for drying is therefore not the ability to oxidize but the possession of a unit molecule with a 'sufficient number and type of reactive centers to permit unrestricted growth in all directions'. In other words, 'the simplest (monomeric) unit should be capable of joining with more than 2 other units'. Only one double bond in each acid radical of a drying oil ordinarily functions as an active center. That is, of several double bonds having 'potential functionality' only one has 'active functionality'. Saponification of polymerized or oxidized drying oils gives dimeric acids regardless of the extent of polymerization of the oil. He has shown geometrically that the alcohol esterified with the drying oil acid must be at least triatomic if a branched, 3-dimensional structure is to be formed. This was confirmed experi-

mentally by the inability of glycol linoleate to dry. Later (3) he suggested that these concepts were sufficient to explain the phenomena for the bodying of drying oils, without recourse to the colloidal considerations.

Another of Bradley's (2,3) investigations was an examination of the isolated fraction from solvent-extracted stand oils and their gels. He obtained evidence that related the several phases not only to the degree of polymerization but to the extent and nature of the intramolecular reactions as well. This work was carried out experimentally using a gelled produce derived from the heat treatment of a mixture of 89% oiticica oil and 11% sardine oil. The gel was extracted with solvents including acetone and the resulting soluble liquid and insoluble solid phases were analyzed for saponification number, acid value, iodine number, molecular weights, refractive indices, and specific gravity. On making a thorough analytical study of the data obtained he found that the gel in esterified glyceride form contained 70% of insoluble solid phase and 30% of soluble liquid phase. Only liquid esters were obtained by saponification, hydrolysis, and reesterification with methanol. These methyl esters were separated into volatile monomeric esters and nonvolatile dimeric esters by distillation. His observation was that the ratio of the monomers to the dimers was markedly different for the two phases of the original gel. Obviously the gelled insoluble phase was more

highly polymerized than the liquid phase'. He showed that the tri-glyceride molecules react intramolecularly and intermolecularly to form dimers, trimers, polymers and eventually polymer ring closures. This theory combined with his original theory of the three dimensional structures formed on polymerization of the oil and resin molecules lead to the suggestion that an aged oleo-resinous film consists of multiples of polymerized molecules intermolecularly connected in ring enclosures which in turn are interconnected to each other forming a continuous network of ring enclosures.

In connection with the intermolecular reactivity which occurs in the polymerization of resins (this is analogous to the same type reaction occurring with the drying oils) Kienle (12) has concluded that (a) organic compounds of high molecular weight are formed only when the interacting molecules are polyactive, (b) the interlinking of the molecules proceeds according to the chance contact of any 2 individual reactive points and (c) the relative sizes and shapes of the reacting molecules and the position of the reacting points largely determine the physical properties of the resulting polymer. He suggested that in a system involving the interaction of polyfunctional molecules, the progress of polymer formation is such that as each intermediate product of polymeric molecule is formed, the functionality of this intermediate product or polymeric molecule should be con-

sidered as if the newly formed molecule were a monomer.

If we consider the oleoresinous film as a complex lattice work of three dimensional oil and resin molecules intermolecularly connected and serving as a potential frame work, we can conceive that the dimeric and monomeric molecules which have not linked themselves in the network are still available as unpolymerized (or low polymerized) liquid partially adsorbed on the polymer surfaces and extractible with solvents. As aging of a film continues, the polymerization continues and the lattice network becomes more complicated with these interwoven fibre-like molecules; thus more insoluble matter is present and less soluble liquid or semiliquid remains. Curves showing the relation between the percent unextractible of the film and the age should show a sharp increase in the 'polymer-content' during the early stages of aging, and a gradual increase later on when the interwoven structure has become so complicated that the chances for functional groups to contact one another is lessened.

The film strength which is related to exposure durability of a film has been measured by distensibility (load-elongation) methods (18). This suggests that the intrinsic life or durability of a film is measurable and can be considered in the light of the film structure theory set forth above. During its early aging periods a film possesses relatively high elastic properties which decrease on continued aging. After the film

has dried sufficiently to possess elasticity, a weak intermolecular network has built up by polymerization to a point where there is an appreciable insoluble portion in the film. On further aging this network has developed more strongly and the elasticity should be even greater. However, on continued aging the intermolecular network has become so complicated by additional polymerization and linkages that the tendency for it to stretch under an applied load is lessened. When a film has aged to the point where its elasticity approaches zero, we would expect it to be a very complex network of polymers unable to withstand external stresses because of its interwoven complexity. These stresses might be set up by elongation tests or they might be set up by those energies which cause ordinary failure on exposure. At this zero point it would be expected that the 'polymer-content' of the film be high and probably on the gradual rise portion of the curve mentioned above.

If this theory be true then we would expect to find the 'polymer-content' of all oleoresinous films to be within a limited range at the exact zero point of failure. Theoretically, the only variations to this would be in the basic differences of the materials used in the formulation and in the ratios in which they are used.

Practically, the determination of the exact age at which the elasticity of a film becomes zero is indeterminable even

if all other conditions are perfectly controlled. However, by the use of curves a close approximation should be obtainable. In conducting this investigation one resin, two oils, and one pigment were aged, elongated, and extracted individually (where possible) and together in different oleoresinous ratios in an effort to obtain data supporting or derating the theory set forth.

RAW MATERIALS

The materials used in preparing the formulations are listed in Table I. The properties of these raw materials are given below.

The linseed oil was a bodied Z-3 oil having an iodine number of 120.3. The china wood or tung oil was A.D.M. No. 50 cal-orized oil having an iodine number of 131.2.

Mineral spirits having a specific gravity of 0.791 and a boiling range of 153-204°C was used in thinning the varnishes and oil formulations. Butyl acetate having a specific gravity of approximately 0.875 and a boiling range of 115-130°C was used as the solvent for the congo spirit varnish. The acetone used as the extracting solvent had a specific gravity of 0.792 and a boiling range of 55.1-57°C.

Numbers 11 and 12 bold amber Congo resin, 'run' at 610°F and having an acetone insolubility of 22%, was the resin used in preparing all formulations.

Pure Rayox grade non-chalking titanium dioxide bulk-ing 0.03118 pounds per gallon having an oil absorption of 24.2 and a specific gravity of 3.88 was used as the pigment in all enamels. The TiO_2 was ground in 65% paste on a laboratory mill at three passes per paste to obtain proper dispersions of the pigment in the oils. The pigment weight ratio was 2.25 lbs. of TiO_2 per 4 lbs. of initial solids present. All enamel formulations were checked for satisfactory dispersions by means of the

microscope.

Liquid Nuodex lead and manganese driers containing 24% and 6% metal, respectively, were added to the varnish and enamel formulations on a metal-to-oil weight basis of 0.60% lead and 0.06% manganese. A 60 gallon lead and manganese drier consisting of linseed oil and rosin was added to the straight oil samples on a volume basis of one part drier to nineteen parts oil. This drier was used because of difficulties in obtaining satisfactory films with straight oil samples containing the Nuodex driers. The errors introduced by this difference in driers can be only slight. In addition to this change in driers it was still necessary to dry the straight tung oil films in an atmosphere of oxygen to prevent gas-checking.

The 8 and 53 gallon length varnishes were prepared by cooking the resin with the oils at 560°F, thinning at 450°F with mineral spirits and filtering at about 200°F. The 16 and 25 gallon length varnishes were prepared by blending the 8 and 53 gallon varnishes in the proper calculated ratios. The enamels were prepared by pigmenting portions of the varnishes.

The formulations are shown in Table II.

TABLE I

RAW MATERIALS

Drying Oils	Resin	Solvents	Driers	Pigment
Z-3 Bodied Linseed	Bold Amber Congo	Mineral Spirits	Nuodex Lead	Rayox Titanium Dioxide
A.D.M. No. 50 Tung		Butyl Acetate	Nuodex Manganese	
		Acetone	Lead and Manganese in Linseed var- nish drier	

TABLE II
FORMULATIONS

Formula Code *	Oil length in gallons	Drying oil	Type of finish	Thinner	Drier	Percent Solids
CL1	33	Linseed	Varnish	M.S.	Nuedex Pb & Mn	51.1
CL2	25	Linseed	Varnish	M.S.	Nuedex Pb & Mn	48.3
CL3	16	Linseed	Varnish	M.S.	Nuedex Pb & Mn	51.5
CL4	8	Linseed	Varnish	M.S.	Nuedex Pb & Mn	51.4
CL5	∞	Linseed	Straight oil	M.S.	Pb & Mn in Linseed Varnish drier	75.1
CT1	33	Tung	Varnish	M.S.	Nuedex Pb & Mn	50.2
CT2	25	Tung	Varnish	M.S.	Nuedex Pb & Mn	50.0
CT3	16	Tung	Varnish	M.S.	Nuedex Pb & Mn	51.7
CT4	8	Tung	Varnish	M.S.	Nuedex Pb & Mn	55.2
CT5	∞	Tung	Straight oil	-	Pb & Mn in Linseed Varnish drier	96.6

* C - designates varnish series, L - linseed oil, T - tung oil, 1 - 33 gallon length, 2 - 25 gallon, 3 - 16 gallon, 4 - 8 gallon, 5 - straight oil.

TABLE II (continued)

FORMULATIONS

Formula Code *	Oil length in gallons	Drying oil	Type of finish	Thinner	Drier	Percent Solids
DLP1	33	Linseed	Enamel	M.S.	Nuedex Pb & Mn	63.0
DLP2	25	Linseed	Enamel	M.S.	Nuedex Pb & Mn	61.2
DLP3	16	Linseed	Enamel	M.S.	Nuedex Pb & Mn	63.7
DLP4	8	Linseed	Enamel	M.S.	Nuedex Pb & Mn	68.3
DLP5	∞	Linseed	Pig. in oil	M.S.	Pb & Mn in Linseed Varnish drier	82.6
DTP1	33	Tung	Enamel	M.S.	Nuedex Pb & Mn	61.5
DTP2	25	Tung	Enamel	M.S.	Nuedex Pb & Mn	61.8
DTP3	16	Tung	Enamel	M.S.	Nuedex Pb & Mn	63.6
DTP4	8	Tung	Enamel	M.S.	Nuedex Pb & Mn	66.3
DTP5	∞	Tung	Pig. in oil	-	Pb & Mn in Linseed Varnish drier	98.7
CS	0	none	Spirit varnish	Butyl acetate	none	42.7

* D - designates enamel series, L - linseed oil, T - tung oil, 1 - 33 gallon length, 2 - 25 gallon, 3 - 16 gallon, 4 - 8 gallon, 5 - straight oil, P - pigment, CS - conge spirit varnish.

EXPERIMENTAL APPARATUS

The apparatus used in this investigation consisted of several standard and several unique pieces of equipment, all of which are described below.

FILM CASTERS. Films were cast with a doctor blade (10) capable of depositing uniformly thick films. The caster is simply an upright piece of steel having spacers at the ends fastened to the blade so as to make a gap-width of 0.01 inch when set upright on a plane. This caster has an overall width of $4\frac{1}{2}$ inches and deposits a film $\frac{3}{8}$ inches wide. All films were cast with this caster by the same operator who used a pulling stroke at a uniform rate of about 18 inches per minute. Films cast by this method dried to a uniform thickness in the range of 0.002 to 0.005 inch depending upon the solid content of the sample. See Figs. 1 and 4.

PANELS. All films were cast on 31 gage coke tin panels 5 X 10 inches in size having $\frac{1}{4}$ inch holes centered $\frac{3}{8}$ inch from the tops. To facilitate clean and uniform films on the tin surface each panel was carefully cleaned with ethyl alcohol and placed upon a leveled plate glass for the film casting. The panels were made to adhere smoothly to the glass surface by spreading a water film between the two surfaces. This was done by placing several drops of water on the glass and firmly pressing the panel upon the two. The films were removed from the tin surface by amalgamation with technical mercury, thus producing free films.

Fig. 1. Casting film on tin panel with doctor blade.

ACCELERATED WEATHERING UNIT. A National Carbon Company Accelerated Weathering Unit operating at 60 amperes and burning Nos. 13 and 22 UCC sunshine carbons was used. This unit weathered 64 3×10 inch panels simultaneously. It was operated at 75°C (107°F) during the dry heat and light portion of the cycle and at $38-40^{\circ}\text{C}$ ($100.4-104.0$) during the moist heat and light portions. A refrigerator maintaining a temperature of -20°C (-4°F) was operated in conjunction with the weathering unit for the cold portion of the cycle. The cycle selected for this investigation is one developed by the Commonwealth Edison Company of Chicago. A calibration of this cycle and unit for outdoor weather in Louisville is in progress at this writing. The continuous daily schedule constituting one cycle is as follows: (Unit is shown in Fig. 3).

4 hours	Light and water spray	10:00 AM- 2:00 PM
5 hours	Light without water	2:00 PM- 7:00 PM
4 $\frac{1}{2}$ hours	Light and water spray	7:00 PM-11:30 PM
4 hours	Water spray alone	11:30 PM- 3:30 AM
3 $\frac{1}{2}$ hours	Rest period	3:30 AM- 7:00 AM
3 hours	Refrigeration	7:00 AM-10:00 AM

OUTDOOR TEST PANEL FENCE. A test fence accomodating 150 test panels was built on the roof of the laboratory building for the purpose of calibrating the accelerated weathering unit. The fence was built so as to give a '45° south' exposure. See Fig. 2.

CONSTANT-TEMPERATURE, CONSTANT-HUMIDITY ROOM. A well weather-stripped room encased on the outside with brick and located on

Fig. 2. Accelerated weathering unit.

Fig. 3. Outdoor exposure fence.

the basement floor of the laboratory building was used for an approximate constant-temperature, constant-humidity room for conditioning the films for the elongation tests. The temperature was maintained in the range of 21.1-29.4°C (70-85°F) and the humidity in the range of 54 to 60% relative humidity. Humidity was controlled by the use of a saturated solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in an open pan as suggested by Gardener (7). Such a solution when contained in an air-tight compartment and held at 21.1°C (70°F) will hold the atmosphere of the enclosure around 54% relative humidity.

FILM CUTTING TEMPLATE. A 6 X 1 X $\frac{3}{8}$ inch bar of cold-rolled steel was polished on one 1 X 6 inch face and used as a template for cutting the film strips used in the elongation tests. See Fig. 4.

MICROMETER. A Randall & Stickney dial gage micrometer was used in determining the film thickness of the test strips for the elongation tests. Each degree on the dial gage reads 0.001 inch thickness. See Fig. 4.

ELONGATION TESTER. A model X-5 Scott Tensile Tester manufactured by the Henry L. Scott Co. of Providence, R.I. was used in determining the tensile strength and elongation of the free films. This tester operates at a constant speed of 12 inches per minute and has a double operating capacity of 0 to 2 pounds and 0 to 10 pounds. See. Fig. 5.

EXTRACTION APPARATUS: Thirty-six Soxhlet extraction units ar-

Fig. 4. View showing micrometer on right, doctor blade in center, steel template on left, and stripped films in background.

Fig. 5. Tensile tester used in making the distensibility tests.

Fig. 6. Extraction units used in extracting the films

ranged in three batteries of twelve units each were used for the film extractions. Each extraction unit consisted of an Erlenmeyer flask and a metal condensing coil which was so constructed that it protruded down within the top of the flask. On the bottom of the condensing coil was suspended the characteristic Soxhlet siphon cup into which was fitted the porous thimble containing the film sample. Each battery was constructed as a long narrow box so as to contain twelve units fitted with holes in the top of the box and twelve 75 watt incandescent lamp heaters fitted in the box directly under the extraction units. Water for the condensers was provided by means of two pipes fixed on the outsides of the box, so that the water cooling system operated in parallel. See Fig. 6.

EXTRACTION THIMBLES. Whattman extraction thimbles 22mm diameter and 80mm long and made of porous parchment paper were used as the receptacles for the film samples in the Soxhlet extraction cups. Each thimble was lined with No. 30 Whattman filter paper in order to protect the thimble for subsequent use. Double thickness thimbles were used whenever a pigmented film was to be extracted.

EXPERIMENTAL PROCEDURE

The general experimental procedure followed in this investigation consisted of casting, aging, inspecting, stripping, conditioning, elongating, and extracting the films produced from the prepared oil, varnish, and enamel formulations. Each step will be explained.

CASTING. Plate glass panels were leveled and a film of water spread over the top surface. Tin panels were thoroughly cleaned on both sides with ethyl alcohol and firmly pressed onto the wetted glass so as to produce adhesion between the two. This facilitated a flat and stationary metal surface. All films were cast with a 0.01 inch doctor blade which deposited films drying to uniform thicknesses of approximately 0.0025 inch. The straight oil films dried thicker because of the high solid content. Each film of a particular sample dried to a uniform thickness of ± 0.0004 inch. However, due to the differences in surface tension and the solid content of the various samples the film thickness varied ± 0.002 inch over the entire investigation. All films were cast by the same operator who cast with a forward pull on the caster of 18 inches per minute. The films were allowed to dry in a quiet atmosphere for two or three days before the next step was commenced. Two films of each formulation were prepared at every casting so as to have a complete set of panels representing every formulation included in every run of the tests which followed.

AGING. The panels were trimmed to $3\frac{1}{4}$ X 10 inches and aged in

the accelerated weathering apparatus for a designated number of cycles. Changes from one period to another within a cycle were made by hand, however, the schedule for changes was adhered to closely.

INSPECTING. At the end of every cycle each panel was carefully inspected for chalking, loss of gloss, checking, cracking, and alligating. Changes in film conditions were recorded. Because of the difficulty in detecting failure by chalking for the non-chalking pigment used, the first definite sign of failure noted was of a checking nature. This is the type of failure referred to in Tables III-VI and in Figs. 7-16.

STRIPPING. After removing a panel from the weathering unit the film was wiped free of water and set in a tilting position with the top end raised about 15° with the horizontal. A small portion of unprotected tin near the top end of the film was wiped clean and a drop of technical mercury from a medicine dropper placed there. The panel was left in this position overnight allowing the amalgamation to take place. The films were then trimmed around the edges of the panel with a razor blade and carefully lifted or stripped free from the panel. The adhesion of films to amalgamated tin is so slight that this stripping process is quite satisfactory for removing films without elongating them.

CONDITIONING. The stripped films were hung on clips in a constant-temperature, constant-humidity room for 36 or more hours

permitting them to reach temperature-humidity equilibrium with the room conditions before testing in the room.

ELONGATING. Two film strips measuring exactly 1 X 6 inches were cut out of each film using a steel template as pattern and a razor blade for the cutter. The strips were measured for minimum thickness with a micrometer. The location of all varying thicknesses was noted. The value corresponding to that location in which the film broke was taken as the film thickness. The two films for each sample as cast furnished four strips per formulation for that particular elongation test. The test performed on each strip consisted of fastening the film between the upper and lower jaws of the tester, measuring the length of film free to stretch between the jaws, reading the initial load on the load scale, applying the load by means of the starter, stopping the loading immediately after the break occurred, remeasuring the length between the jaws, and reading the final load on the load scale. From the tensile strength and percent elongation data thus obtained, the calculated values for the satisfactory pulls were averaged and the averages taken as the distensibility values.

EXTRACTING. The films were then cut up into fine bits (and ground in a mortar with a pestal when possible) in preparation for extraction with acetone. Before the fine film particles were placed in the extraction thimbles it was necessary to extract the thimbles empty permitting them to attain a fibre free and insoluble con-

dition, then heat them in an oven at 105°C (221°F) for two hours, cool them to room temperature in a dessicator, and weigh them for tare weight. Samples of about 2 grams in weight were carefully placed in the thimbles and therein extracted for approximately two weeks time. Several times during the extraction period the thimbles were dried, cooled, and weighed in order to determine the progress of the extraction. All weighings were made with the thimble in a weighing bottle on an analytical weighing balance. Two empty thimbles were extracted, heated, cooled, and weighed as blank thimbles in every set of samples extracted. This was done so as to reduce incurring errors resulting from any uncontrollable weight changes during the conditioning and weighing of the thimbles. The average of the changes in weight of the blanks over their original weights was taken as the blank correction for that particular weighing and was applied to all sample weights in calculating the percent of sample unextracted.

DATA AND RESULTS

The tensile strength, percent elongation, and percent unextractable data for the oil, varnish, and enamel films are given in Tables III-VI. Table VII gives the extraction data for the congo resin films. Table VIII gives the ratio in which the oils and resin were used and the percent unextractable when failure occurs.

The tensile strength of a film was obtained by dividing the ultimate load required for the break by the film thickness. The films were cut 1 inch wide, consequently, the values are reported as pounds per square inch. Percent elongation was calculated by dividing the difference of the initial length and multiplying by 100. It should be noted here that the hand operated release on the tensile tester made it impossible to stop the measuring mechanism instantaneously with the break, consequently, all readings are subject to a positive error of 0.07 inch or less. This error amounts to about 2% or less. Percent unextractable was calculated by dividing the dry insoluble portion of the film by the weight of original dry sample and multiplying by 100.

The astericks in the tables and the short perpendicular lines crossing the curves in the figures indicate the approximate points of definite film failure as determined by inspection.

Figures 7-17 are curves obtained by plotting the percent of film unextractable versus age and versus percent elongation. No curves were drawn showing a relation of tensile strength.

TABLE III

Distensibility and Percent Unextractible of Linseed Varnishes

Formula (oil length)		0	1	2	Cycle Number							
					3	4	5	6	7	8	9	10
CL1 (33)	Ten. Strength	-	-	417	417	314	400	562	-	320	* -	too
	% Elongation	-	-	4.1	3.8	3.8	2.3	1.6	-	1.8	-	brittle
	% Unextract.	16.5	-	63.2	-	-	-	86.4	-	84.8	-	80.6
CL2 (25)	Ten. Strength	-	-	350	282	285	314	552	* -	too	-	too
	% Elongation	-	-	3.1	2.7	2.5	1.6	1.7	-	brittle	-	brittle
	% Unextract.	16.3	-	65.2	-	-	-	78.5	-	71.2	-	82.7
CL3 (16)	Ten. Strength	-	-	281	264	307	* 221	too	-	too	-	too
	% Elongation	-	-	2.0	1.8	1.5	1.2	brittle	-	brittle	-	brittle
	% Unextract.	14.5	-	65.1	-	-	-	73.5	-	60.1	-	81.0
CL4 (8)	Ten. Strength	-	* -	too	too	-	-	-	-	-	-	-
	% Elongation	-	-	brittle	brittle	-	-	-	-	-	-	-
	% Unextract.	7.6	-	67.8	60.6	-	-	-	-	-	-	-
CL5 (stra. oil)	Ten. Strength	-	-	17.1	-	96	-	88	-	111	-	214
	% Elongation	-	-	45.2	-	57.3	-	40.7	-	50.1	-	62.1
	% Unextract.	22.5	-	81.5	-	79.9	-	86.8	-	85.8	-	79.9

* Indicates first point of checking failure.

TABLE IV

Distensibility and Percent Unextractible of Tung Varnishes

Formula (oil length)		0	1	2	Cycle Number		5	6	7	8	9	10
CT1 (33)	Ten. Strength	-	-	940	706	373	538	489	-	* 317	-	too
	% Elongation	-	-	14.3	5.6	4.0	1.8	2.5	-	1.8	-	brittle
	% Unextract.	22.8	-	75.5	-	66.3	-	77.5	-	67.5	-	83.6
CT2 (25)	Ten. Strength	-	-	542	419	389	395	414	* -	too	-	too
	% Elongation	-	-	3.2	2.1	3.0	1.8	1.8	-	brittle	-	brittle
	% Unextract.	14.7	-	67.4	-	-	-	76.4	-	77.2	-	84.3
CT3 (16)	Ten. Strength	-	-	283	278	203	* 333	329	-	too	-	339
	% Elongation	-	-	1.5	1.5	1.6	2.1	2.2	-	brittle	-	1.8
	% Unextract.	10.9	-	65.5	-	60.0	-	72.5	-	74.4	-	83.6
CT4 (8)	Ten. Strength	-	-	* too	too	-	--	-	-	too	-	-
	% Elongation	-	-	brittle	brittle	-	-	-	-	brittle	-	-
	% Unextract.	1.8	-	51.0	62.5	-	-	-	-	71.1	-	-
CT5 (stra. oil)	Ten. Strength	-	-	19	-	75.9	-	131	-	96	-	168
	% Elongation	-	-	37.4	-	48.6	--	48.0	-	38.2	-	42.7
	% Unextract.	4.2	-	80.0	-	80.2	-	84.1	-	83.8	-	87.0

* Indicates first point of checking failure.

TABLE V

Distensibility and Percent Unextractible of Linseed Enamels

Formula (oil length)		0	1	2	Cycle Number		3	4	5	6	7	8	9	10
DLP1 (33)	Ten. Strength -	-	-	413	320	347	463	500	-	* 430	-	810		
	% Elongation -	-	-	21.4	34.2	11.0	2.7	3.1	-	2.8	-	4.4		
	% Unextract. 55.7	-	-	75.7	-	72.7	-	82.7	-	84.7	-	86.3		
DLP2 (25)	Ten. Strength -	-	-	526	329	315	312	493	* -	too	-	691		
	% Elongation -	-	-	13.1	24.0	10.7	1.8	2.8	-	brittle	-	3.1		
	% Unextract. 54.1	-	-	77.6	-	-	-	78.5	-	72.7	-	88.3		
DLP3 (16)	Ten. Strength -	-	-	217	221	-	* too	-	-	too	-	319		
	% Elongation -	-	-	1.8	2.6	-	brittle	-	-	brittle	-	1.8		
	% Unextract. 49.5	-	-	71.0	73.8	-	84.5	-	-	65.6	-	84.0		
DLP4 (8)	Ten. Strength -	-	too	* too	too	-	-	-	-	-	-	-		
	% Elongation -	-	brittle	brittle	brittle	-	-	-	-	-	-	-		
	% Unextract. 43.1	-	61.3	58.5	65.6	-	-	-	-	-	-	-		
DLP5 (pig. oil)	Ten. Strength -	-	-	110	-	110	-	155	-	139	-	187		
	% Elongation -	-	-	60.6	-	53.4	-	55.8	-	50.6	-	44.5		
	% Unextract. 48.3	-	-	79.7	-	81.4	-	86.5	-	87.1	-	89.7		

* Indicates first point of checking failure.

TABLE VI

Distensibility and Percent Unextractible of Tung Enamels

Formula (oil length)	Cycle Number										
	0	1	2	3	4	5	6	7	8	9	10
DTP1 Ten. Strength -	-	-	601	535	400	464	629	* -	642	-	1152
(33) % Elongation -	-	-	19.5	60.9	16.2	4.4	9.4	-	3.1	-	6.3
% Unextract. 39.2	-	-	73.2	-	75.0	-	84.6	-	79.7	-	90.4
DTP2 Ten. Strength -	-	-	609	406	349	* 413	499	-	-	-	1018
(25) % Elongation -	-	-	5.5	23.3	3.4	3.9	3.4	-	-	-	3.6
% Unextract. 54.0	-	-	75.2	-	-	-	79.0	-	79.8	-	88.2
DTP3 Ten. Strength -	-	-	187	* 298	242	235	295	-	224	-	300
(16) % Elongation -	-	-	2.0	5.9	2.1	1.4	1.8	-	1.7	-	1.9
% Unextract. 54.4	-	-	69.7	-	-	-	81.2	-	70.2	-	87.2
DTP4 Ten. Strength -	-	too	* too	too	-	-	-	-	-	-	-
(8) % Elongation -	-	brittle	brittle	brittle	-	-	-	-	-	-	-
% Unextract. 45.0	-	67.0	62.2	72.4	-	-	-	-	-	-	-
DTP5 Ten. Strength -	-	-	128	-	118	-	175	-	199	-	330
(pig. % Elongation -	-	-	35.5	-	30.8	-	38.3	-	40.5	-	45.3
oil) % Unextract. 35.7	-	-	85.7	-	87.4	-	86.7	-	85.0	-	90.5

* Indicates first point of checking failure.

TABLE VII
Extraction of Congo Resin

Cycle No.	Percent Unextractible
0	22.0
1	56.2
2	63.0
3	-
4	63.6
5	66.4
6	54.3

A Unextractable vs Age - 33 gal. varnish

B Unextractable vs Age - 33 gal. enamel

C Unextractable vs Elongation - 33 gal. varnish

D Unextractable vs Elongation - 33 gal. enamel

Note: I indicates point at which definite failure first appeared

FIG. 7 PERCENT UNEXTRACTABLE vs AGE AND ELONGATION
FOR 33 GAL. LINSEED VARNISH AND ENAMEL

FIG. 8 PERCENT UNEXTRACTIBLE vs AGE AND ELONGATION
FOR 25 GAL. LINSEED VARNISH AND ENAMEL

A Unextractable vs Age - 16 gal. varnish

B Unextractable vs Age - 16 gal. enamel

C Unextractable vs Elongation - 16 gal varnish

D Unextractable vs Elongation - 16 gal enamel

Note: I indicates point at which definite failure first appeared

FIG. 9 PERCENT UNEXTRACTIBLE vs AGE AND ELONGATION
FOR 16 GAL. LINSEED VARNISH AND ENAMEL

FIG. 10 PERCENT UNEXTRACTABLE vs AGE FOR
8 GAL. LINSEED VARNISH AND ENAMEL

FIG. 11 PERCENT UNEXTRACTABLE vs AGE AND ELONGATION
FOR STRAIGHT LINSEED OIL FILMS

- Note: I indicates point at which definite failure first appeared

FIG. 12 PERCENT UNEXTRACTIBLE vs AGE AND ELONGATION
FOR 33 GAL. TUNG VARNISH AND ENAMEL

A Unextractable vs Age - 25 gal. varnish

B Unextractable vs Age - 25 gal. enamel

C Unextractable vs Elongation-- 25 gal. varnish

D Unextractable vs Elongation-- 25 gal. enamel

Note: I indicates point at which definite failure first appeared

FIG. 13 PERCENT UNEXTRACTABLE vs AGE AND ELONGATION
FOR 25 GAL. TUNG VARNISH AND ENAMEL

A Unextractable vs Age - 16 gal. varnish

B Unextractable vs Age - 16 gal. enamel

C Unextractable vs Elongation - 16 gal. varnish

D Unextractable vs Elongation - 16 gal. enamel

Note: I indicates point at which definite failure first appeared

FIG. 14 PERCENT UNEXTRACTABLE vs AGE AND ELONGATION
FOR 16 GAL. TUNG VARNISH AND ENAMEL

A 8 gal. varnish

B 8 gal. enamel

FIG. 15 PERCENT UNEXTRACTABLE VS AGE FOR
8 GAL. TUNG VARNISH AND ENAMEL

FIG. 16 PERCENT UNEXTRACTIBLE vs AGE AND ELONGATION
FOR STRAIGHT TUNG OIL FILMS

FIG. 17 PERCENT UNEXTRACTABLE vs AGE FOR
CONGO RESIN FILM

TABLE VIII
Percent Unextractible of Films at Failure

Varnish	% Oil	% Resin	% Unex- tractible	Enamel	% Oil	% Resin	% Unex- tractible
33 Lin.	72.5	27.5	73.0	33 Lin.	82.5	17.5	74.0
25 Lin.	66.6	33.3	80.0	25 Lin.	78.7	21.3	83.0
16 Lin.	56.2	43.8	72.0	16 Lin.	72.0	28.0	80.0
8 Lin.	39.0	61.0	36.0	8 Lin.	61.0	39.0	63.0
33 Tung	72.5	27.5	75.0	33 Tung	82.5	17.5	82.0
25 Tung	66.6	33.3	77.0	25 Tung	78.7	21.3	80.0
16 Tung	56.2	43.8	68.0	16 Tung	72.0	28.0	71.0
8 Tung	39.0	61.0	52.0	8 Tung	61.0	39.0	69.0

DISCUSSION OF RESULTS

The curves representing polymerization rates for the varnishes and enamels (curves A & B in Figs. 7-16) tend to rise with a relatively steep slope during the early life of the film and gradually taper off asymptotically as aging continues. The failure points on these curves occur nearer the asymptotic values as the oil lengths increase. This is shown directly on the varnish and enamel curves of Figs. 7-10 and 12-15 and indirectly by curves A and B of Figs. 11 and 16 where no failure occurred in 10 cycles for infinite oil length samples (straight oil) and on curve A of Fig. 17, where failure of the straight resin sample occurred before the first cycle was completed.

The extraction data was obtained under such conditions that an error of $\pm 3\%$ does not seem unreasonable from the experimental point of view. The varnish and enamel curves A and B (Figs. 7-9, 12-14) of the 33, 25, and 16 gallon lengths for both oils have two things in common that appear conclusive. Each enamel curve tapers slower but to approximately the same asymptotic value as its corresponding varnish curve. Thus the change in rate of polymerization is slower in the enamels than in the varnishes. Also, the failure point on each enamel curve occurs within two or less cycles less time than for the corresponding varnish but at the same unextractable value. It appears that not only does failure occur in a film when polymerization has gradually reached a definite point but the pigment incorporated in a varnish to form the enamel is

definitely counted as 'polymer' and because of its presence will probably decrease the durability of the film as a protective coating. This supports the theory presented in that the pigment bound in the structural network is sharing in the complexity of the film and reducing the number of chance contacts that the functional groups have with one another. This also explains why the rate of polymerization was slower in the enamels than in the case of the varnishes. Apparently the percent of 'polymer' contained in the various formulations when failure occurred vary with the oil selected and with the ratio in which it is used with the resin. See Table VIII for these values. It is important to bear in mind that the pigment was added to the varnishes on a solids basis thus shortening the actual oil length of the enamel samples. Had the enamels been adjusted back to the proper oil lengths the age differences in failure occurrences would probably have been diminished to near zero.

If the error in the distensibility tests is considered $\pm 2\%$ and the elongation curves are corrected by this value (curves C and D, Figs. 7-16) so as to move the left coordinate to the right 2% (or less) it can be seen (where elongation curves were obtained) that the new zero elongation value occurs within the allowable range of the previously determined polymer value at which failure occurred. For example, shift the left vertical coordinate of Fig. 7 to the right 2 units (2%), curves C and D cross this axis at 72% and 78% respectively and are approximately within $\pm 3\%$ of the 75% polymer

value which was previously located by inspection. This shows a fair correlation between the two methods employed to determine film failure.

Correlation is difficult for the tensile strength data because of its fluctuations. This can be accounted for by the inaccuracy of the film thicknesses and their measurement. Schuh and Theurer (17) have stated several variables that determine distensibility which aid in explaining what may have caused the discrepancies in this data. They are: (a) composition of the film-forming material, (b) thickness of the film, (c) age and history of the film, (d) temperature and humidity at time of test, (e) and the rate of stress application.

A set of composite curves was developed to determine what relation exists between the resin, oil and pigment on polymerization. Each curve (Figs. 18-25) is based on the polymerization curves of the individual materials in their proper ratios as used in formulating the varnishes and enamels. Actually they are the results of adding the curves of the individual materials which have been multiplied by the proper ratio. For example, a so-called composite polymerization curve for a 33 gallon linseed varnish would be an additive curve obtained by multiplying the polymerization data (percent unextractible data at various ages) for the resin by the ratio in which the resin occurs in the solid content of an actual 33 gallon varnish and adding to this data, at the proper aging

periods, the polymerization data for the straight linseed oil which has been multiplied by its occurring ratio. Curve A of Fig. 18 was obtained by multiplying curve A of Fig. 7 by 72.5% (the ratio of oil in the solid content of a 33 gallon varnish, see Table VIII) and adding to it curve A of Fig. 17 which has been multiplied by 27.5%. In other words, the actual curves of the individual materials were diminished by that fraction in which the materials appear in the combined formulations afterwhich the resulting curves were added together. Each composite enamel curve is composed of a pigmented oil curve and a resin curve obtained in a similar manner.

By comparing the composite curves with their corresponding varnish and enamel curves (compare Figs. 18-25 with Figs. 7-10 and Figs. 12-15) it is observed that they are in general analogous, having similar curvature and comparable asymptotic values. This leads to the conclusion that the polymerization occurring in the combined formulations is no different from that occurring in the individual materials. This suggests that the degree of polymerization of a film forming material at a given age can be predetermined by use of previously determined information on the basic materials used. Where the point of failure falls on the composite curve thus produced can not be determined by this procedure developed thus far.

The pigment used in this investigation was inert. Whether a reactive pigment would behave differently is not within the scope of this investigation.

FIG. 18.. COMPOSITE CURVES FOR 33 GAL. LINSEED VARNISH AND ENAMEL

FIG. 19 COMPOSITE CURVES FOR 25 GAL. LINSEED VARNISH AND ENAMEL

FIG. 20 COMPOSITE CURVES FOR 16 GAL. LINSEED VARNISH AND ENAMEL

A 8 gal. varnish

B 8 gal. enamel

FIG. 21 COMPOSITE CURVES FOR 8 GAL. LINSEED VARNISH AND ENAMEL

A 33 gal. varnish

B 33 gal. enamel

FIG. 22 COMPOSITE CURVES FOR 33 GAL. TUNG VARNISH AND ENAMEL

A 25 gal. varnish

B 25 gal. enamel

FIG. 23 COMPOSITE CURVES FOR 25 GAL. TUNG VARNISH AND ENAMEL

FIG. 24 COMPOSITE CURVES FOR 16 GAL. TUNG VARNISH AND ENAMEL

FIG. 25 COMPOSITE CURVES FOR 8 GAL. TUNG VARNISH AND ENAMEL

CONCLUSIONS

Results of the investigation of studying the effect of aging on the distensibility and unextractible properties of oleoresinous film structures lead to the following conclusions:

(1) By extracting films of the basic materials, the procedure developed can be used to predetermine the rate of polymerization curves for oleoresinous films provided any pigments used are inert and the oil length of the varnish or enamel is sufficiently long to withstand several accelerated aging periods.

(2) Film failure occurs when the degree of polymerization has reached approximately 70-80%, however, the procedure as developed is incapable of predicting the expected durability of oleoresinous films.

(3) Oleoresinous film structure is apparently of such a nature that the molecules orient themselves during the aging process to impart elasticity to the film during the early stages of polymerization and brittleness during the last stages. Thus film failure occurs when the polymerization has proceeded to such an extent that the film has lost its elastic properties.

(4) An enamel and a varnish composed of the same materials and constituting approximately the same oil length fail at the same degree of polymerization, however, the enamel polymerizes more slowly.

(5) Inert pigment in enamels must be counted as 'polymer' in an enamel film.

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