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A study of oleoresinous film structure.

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UNIVERSITY OF LOUISVILLE

A STUDY OF OLEORESINOUS FILM STRUCTURE

A Thesis

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of the Graduate School
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By

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A STUDY OF OLEORESINOUS FILM STRUCTURE

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Director R. C. Ernst

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LIST OF SYMBOLS

Designation	Sample Varnish
LE1	16 gallon Linseed Oil-Ester Gum Varnish
LE2	25 " " " " " "
LE3	33 " " " " " "
LN1	16 gallon Linseed Oil-Nevillite Varnish
LN2	25 " " " " "
LN3	33 " " " " "
LB1	16 gallon Linseed Oil-Bakelite Varnish
LB2	25 " " " " "
LB3	33 " " " " "
LA1	16 gallon Linseed Oil-Glycerol Phthalate Varnish
LA2	25 " " " " " "
LA3	33 " " " " " "
TE1	16 gallon Chinawood Oil-Ester Gum Varnish
TE2	25 " " " " " "
TE3	33 " " " " " "
TN1	16 gallon Chinawood Oil-Nevillite Varnish
TN2	25 " " " " "
TN3	33 " " " " "
TB1	16 gallon Chinawood Oil-Bakelite Varnish
TB2	25 " " " " "
TB3	33 " " " " "
DE1	16 gallon Castor Oil-Ester Gum Varnish
DE2	25 " " " " " "
DE3	33 " " " " " "
DN1	16 gallon Castor Oil-Nevillite Varnish
DN2	25 " " " " "
DN3	33 " " " " "
DB1	16 gallon Castor Oil-Bakelite Varnish
DB2	25 " " " " "
DB3	33 " " " " "
DA2	25 gallon Castor Oil-Glycerol Phthalate Varnish
DA3	33 " " " " " "

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ABSTRACT

This investigation is the second in a series whose purpose is to establish a sound basis for formulating oleoresinous coatings. Variation in the chemical type of resin used in the formulations, and the study of the polymerization and distensibility effects accompanying these variations was the basis for the investigation. The change in polymerization and distensibility in the aging film was correlated with the durability of the film as determined by accelerated weather exposure.

The generalization made in the initial investigation regarding the failure of an oleoresinous film when the polymer content reached a definite value, was shown to be in error. The durability of an oleoresinous film is apparently not only a function of the formation of a three-dimensional structure in the film, but must also be considered as being dependent upon other factors not yet known.

INTRODUCTION

This investigation is the second in a series whose purpose is to study oleoresinous film structure so as to establish a sound basis for formulating oleoresinous coatings. The assumption is made that the failure of an oleoresinous film is due to certain conditions present in the film at the time of failure, and that these conditions are caused by a change in the polymer-plasticizer ratio in the film. It is proposed to study the change in this ratio throughout the life of the film, and to correlate the change in the polymer content with the durability of the coating as measured by the distensibility of the film.

The term polymer is used to denote that phase of the film composed of molecules of oil and resin which are so highly polymerized that they are insoluble in acetone. The remainder of the film which is soluble in acetone, and which imparts flexibility to the film, is considered as plasticizer. It is assumed that a minimum allowable concentration of plasticizer is necessary in a durable film.

Ernst and McQuilkin (1) began this investigation on oleoresinous film formulated with bodied linseed oil, calorized chinawood oil, and congo resin. The present investigation is an extension of their work to coatings formulated with these oils and dehydrated castor oil, and various types of synthetic resins. These resins include a phenol-formaldehyde resin, an ester gum, an oil-modified alkyd resin, and a cyclo-paraffin-naphthene polymer.

The experimental procedure developed by Ernst and McQuilkin was continued using certain modifications indicated by their work.

HISTORICAL

Ernst and McQuilkin (1) investigated the changes taking place in the polymer-plasticizer ratio of oleoresinous films formulated with bodied linseed oil and congo resin, and with calorized chinawood oil and congo resin, after successive periods of aging. They measured the distensibility of these films, and showed that failure occurred when the polymer content reached 70-80 per cent, and when the distensibility of the films was less than one per cent. From these observations, they concluded that during the life of an oleoresinous film, a complicated network of three-dimensional oil and resin molecules is formed, and that the formation of this network gradually decreases the elasticity of the film until failure occurs. They also observed that the polymerization rates of oleoresinous films could be determined by extracting films of the basic materials provided that these materials are not reactive.

Various other investigators have studied the mechanism of the formation and deterioration of oleoresinous films. Overholt and Elm (2) exposed simple methyl esters of unsaturated fatty acids to ultra-violet light for various lengths of time and analyzed the resulting films to determine the progress of oxidation and polymerization. They used cryoscopic molecular weight determinations and viscosity measurements to study the rate of polymerization of the films, but were unable to correlate the results obtained by the two methods. In later studies (3,4) with glycol and glycerol esters of the unsaturated fatty acids, they observed that the rate of polymerization is greater in the earlier stages of drying with these esters than it is in the case of the more simple esters.

Long and McCarter (5) investigated the aging of pure trilinoleic and trilinolenic glycerides, and concluded that drying of these esters was principally a matter of colloidal association of high-molecular particles. They showed that the separation of plasticizer from polymer in a dried film may be accomplished by extraction with acetone.

Bradley and Pfann (6) studied the heat-bodying of oils and concluded that both intermolecular and intramolecular reactions proceed, and partial thermal decomposition of the esters also occurs. They separated the insoluble phase of an oil gel from its adsorbed soluble phase, and by analytical methods showed that the insoluble phase consisted of a highly polymerized material composing 70 per cent of the weight of the gel.

Rose and Bolley (7) divided linseed films into three components, liquid, adsorbed liquid, and solid. They asserted that the physical nature of the film is dependent chiefly upon the relative proportions in which the components exist in the film. Linolenic glycerides and linseed oil films were aged and extracted with acetone. It was found that the concentration of the solid phase increased and the concentration of the liquid phase decreased as aging progressed. The unpolymerized and unassociated liquid which was not adsorbed was removed by extraction, but the adsorbed liquid was probably only partially removed.

Shuey (8) studied the influence of resins on the heat-bodying of varnish oils. From his experiments he concluded that the course of change during the heat-bodying of oils is greatly influenced by the presence of resins, and he classified resins into three groups depending upon their reactivity. Group one included heat - hardenable resins which so exceed the oil in polymerization rate that too great a body is obtained before the oil component of the varnish has attained any appreciable degree of polymerization. Group two included non-heat-hardenable resins which body at approximately the same rate as the oil. Group three included the resins which exercise a retarding influence on the polymerization of the oil. Shuey observed that resins seldom form true solutions in oils, and that colloidal effects often overshadow chemical reaction effects.

THEORETICAL

The mechanism of drying of the unsaturated oils is generally agreed to be a combination of oxidation and polymerization or association of the oil molecules to form a solid, partially insoluble film.

Morrell and Marks (9) postulate that the oxidation of the drying oils passes through a peroxide formation to the ketone and aldehyde and finally to the hydroxyl linkages, the unsaturated bonds of the oils being the important factors in the oxidation. Long's (10) studies on the oxygen absorption of trilinolenic glycerides led him to state that drying is a colloidal association process. He neglects double-bond-polymerization in favor of a two-stage drying process. In the first stage, oxygen is rapidly absorbed forming polar molecules, the polar bonds then associating over a longer period of time to give a solid, insoluble phase, and an adsorbed liquid phase.

Kienle (11) and Carothers (12) observed that polymerization is the ordinary reaction of organic chemistry which proceed in multiple fashion because of the multiplicity of reactive or functional groups present in the structure of the polymerizing substance. They postulated that the number of reactive groups determines the formation of a two-dimensional linear or a three-dimensional (cross-linked) polymer. This theory considers linear polymers as soluble and fusible, and cross-linked polymers as insoluble and infusible.

Bradley (13) extended this general polymerization theory and applied it to the drying of unsaturated oils and resins. He stated that the molecules of the soluble oils and resins have linear, two-dimensional structures, which on drying are converted to the three-dimensional structures. The main requirement of drying is therefore not the ability to oxidize but the possession of a molecule with sufficient reactive centers to permit unrestricted growth. Bradley showed that the drying oils must be formed from trihydric alcohols in order that a three-dimensional structure be formed.

In collaboration with Pfann, Bradley (6) investiaged an oil gel formed by overbodying a mixture of oiticica and sardine oils. The gel consisted of a solid, insoluble phase amounting to 70 per cent of the gel, and a soluble , liquid phase. Analysis of the insoluble phase showed that the molecular weight exceeded the theoretical limit for a purely intermolecular addition of triglyceride esters. From this Bradley concluded that intramolecular additions must also have occurred, which would involve ring closures of the triglyceride polymers.

The polymerization of resins is analogous to the reactions taking place in the polymerization of the drying oils. Kienle (14) concluded from his observations that organic compounds of high molecular weight are formed only when the interacting molecules are polyfunctional. The interlinking of the molecules proceeds according to the chance contact of any two individual reactive points, and 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.

Ernst and McQuilkin (1) applied these principles to the aging of oleoresinous films. They considered the film as a complex lattice-work of three-dimensional oil and resin molecules intermolecularly and intramolecularly connected and serving as a potential framework for the monomeric and dimeric molecules which are still present in the low-polymerized liquid phase. As the aging of the film continues, the lattice-work becomes more complicated with these interwoven fibre-like molecules, and the amount of insoluble polymer increases. Thus they reasoned that the rate of polymerization is higher during the early life of the film since more functional groups are present and the chances of contact between these groups are greater.

Ernst and McQuilkin considered the distensibility of the film as a function of the extent to which polymerization has progressed. A fresh film contains only a small per cent of highly polymerized material, and rigid network of polymer has not been developed. Thus the film is highly elastic in the early stages of drying. After aging has progressed further, the lattice-work of highly-polymerized molecules has been built up and the film is less elastic. When a complex network of polymer is present, the film is no longer able to withstand stress and failure occurs.

On the basis of this theory, the polymer content of all films at the point of failure would be approximately equal or within a limited range. Deviations from the end point would be caused by differences in the type of materials used and by varying the proportions in which the oil and resin exist in the film.

RAW MATERIALS

The materials selected for the preparation of the varnishes used in this investigation were typical drying oils and several synthetic resins chosen particularly because of their variation in oil reactivity and chemical type. The oils were Z-3 bodied linseed oil, calorized ADM #50 chinawood oil, and dehydrated castor oil (Synthenol). The resins chosed were ester gum, a phenol-formaldehyde resin (Bakelike #254), a cycloparaffin-naphthene polymer (Nevillite #2), and an oil modified glycerol phthalate. Each oil was cooked with each resin in 16, 25, and 33 gallon lengths, with two exceptions. The 16 gallon combination of dehydrated castor oil and glycerol phthalate did not produce a varnish that was representative of the class, and the chinawood oil-modified glycerol phthalate varnishes were not practicable.

The varnish formulations, except for the Bakelite finishes, were thinned with mineral spirits. Xylol was used in the Bakelite varnishes because of the incompatibility of this resin and mineral spirits.

Regular liquid Nuodex lead, manganese, and cobalt driers were added to the varnish formulations on the basis of 0.3% lead, 0.02% manganese, and 0.015% cobalt. The oil content of the varnishes was the base for the drier addition.

The varnish formulations are shown completely in Table I.

TABLE I

Formulation of Varnish Samples

Sample	Oil	Resin	Thinner	% Solids
LE1	Linseed	Ester Gum	Mineral Spirits	46.8
LE2	"	"	"	50.1
LE3	"	"	"	50.3
LN1	"	Nevillite #2	"	49.8
LN2	"	"	"	50.0
LN3	"	"	"	50.8
LA1	"	Glycerol Phthalate	"	45.0
LA2	"	"	"	74.3
LA3	"	"	"	89.0
LB1	"	Bakelite #254	Xylol	50.8
LB2	"	"	"	50.0
LB3	"	"	"	49.3
TE1	Chinawood	Ester Gum	Mineral Spirits	51.3
TE2	"	"	"	50.0
TE3	"	"	"	49.9
TN1	"	Nevillite #2	"	50.2
TN2	"	"	"	50.0
TN3	"	"	"	51.7
TB1	"	Bakelite #254	Xylol	49.9
TB2	"	"	"	50.3
TB3	"	"	"	54.8
DE1	Castor	Ester Gum	Mineral Spirits	50.6
DE2	"	"	"	50.2
DE3	"	"	"	49.8
DN1	"	Nevillite #2	"	53.0
DN2	"	"	"	50.0
DN3	"	"	"	51.3
DA2	"	Glycerol Phthalate	"	47.3
DA3	"	"	"	51.8
DB1	"	Bakelite #254	Xylol	48.4
DB2	"	"	"	49.5
DB3	"	"	"	49.5

EXPERIMENTAL APPARATUS

The apparatus required in this investigation consisted chiefly of an extraction battery, a distensibility tester, and an accelerated weathering unit. Other equipment included doctor blades for casting films, and panels upon which the films were cast.

FILM CASTERS AND PANELS.

The sample films for the investigation were cast on tin-coated panels with a doctor-blade having a spacing of 0.008 inches. The panels were five by ten inches in size and of #31 gauge thickness (See Fig. 1).

ACCELERATED WEATHERING UNIT.

Rapid weathering of the varnish films was secured by means of an Everready Accelerated Weathering Unit Model X-1, manufactured by the National Carbon Company. The unit is built in the form of a cylindrical, copper-coated, vertical steel shell, inside of which a panel rack is placed. This rack, which has a carrying capacity of sixty-four three and a half by ten inch panels, rotates once in two hours.

The weathering effect of rain is simulated in the unit by a fine water spray which is directed against the panels. Ultra-violet radiation is produced by two carbon arcs which operate alternately for a continuous ten-hour period. The combination of the heat and the radiation from the arc, and the low temperature and water from the

Fig. 1. Casting Film on Tin Panel with Doctor Blade.

spray effect weathering by rapid temperature change and a breakdown of the film material.

A photograph of the weathering unit is shown on page 16.

REFRIGERATING CABINET.

A refrigerating cabinet was operated in conjunction with the weathering unit to produce the weathering effect of extreme low temperature on the varnish films. The cabinet was cooled by means of the expansion of ammonia in coils.

MICROMETER.

The thickness of the free varnish films was measured with a Randall and Stickney platform micrometer (Fig. 3). The micrometer is graduated in thousandths of an inch and readings can be interpolated to ten-thousandths of an inch.

DISTENSIBILITY TESTER.

The Scott Distensibility Tester Model X-5 (Fig. 4) was used to determine the per cent elongation and the tensile strength of the films. The film sample was held between two clamps; the lower clamp being connected to a drive mechanism which produced a constant speed of pull of two inches per minute, and the upper clamp being balanced by weights which actuated a load recording pointer and dial. The elongation of the film was obtained by subtracting the initial length of the film sample (measured between the clamps) from the distance between the clamps at the breaking point of the film.

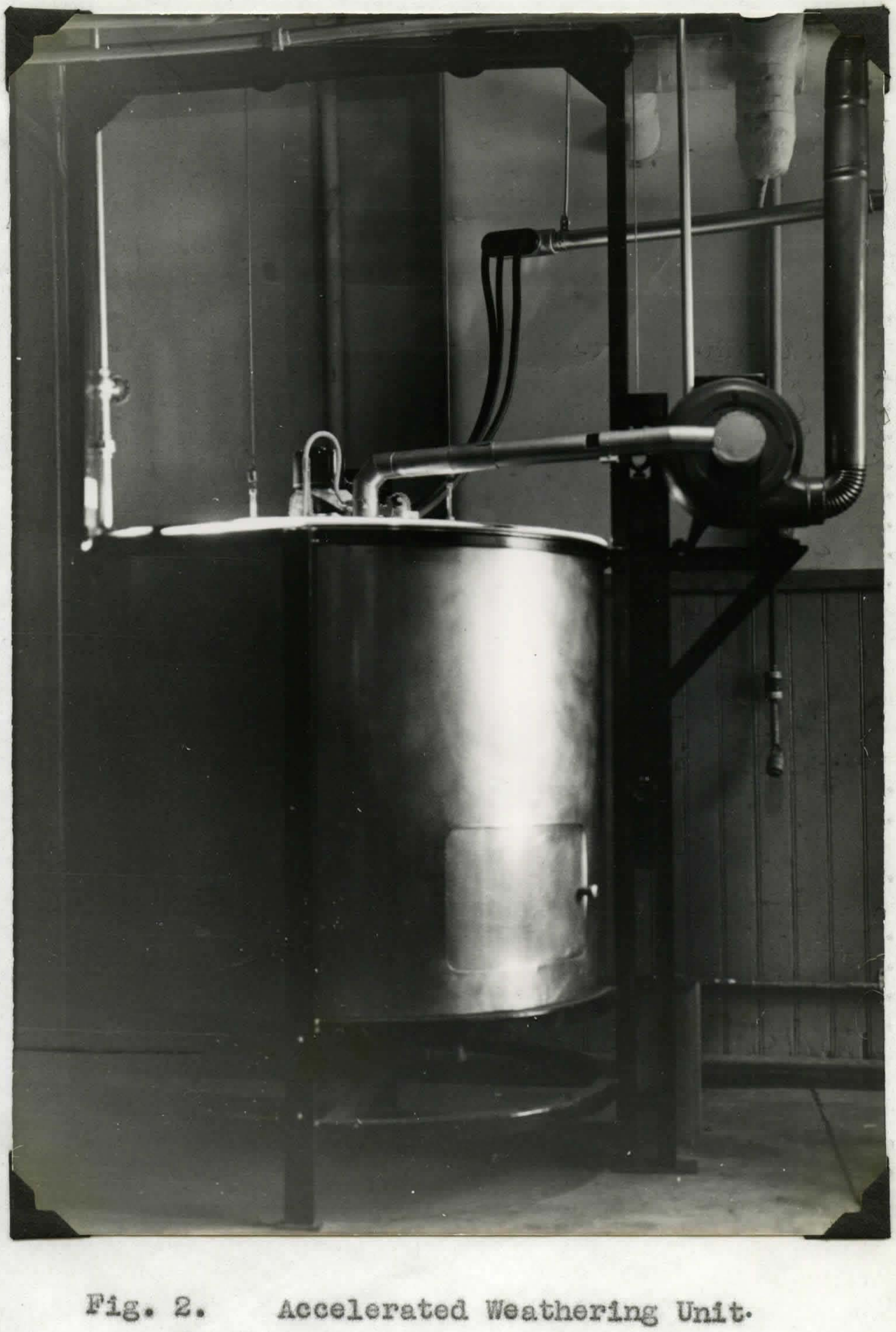

Fig. 2. Accelerated Weathering Unit.

Fig. 3. Micrometer for Measuring Film Thickness.

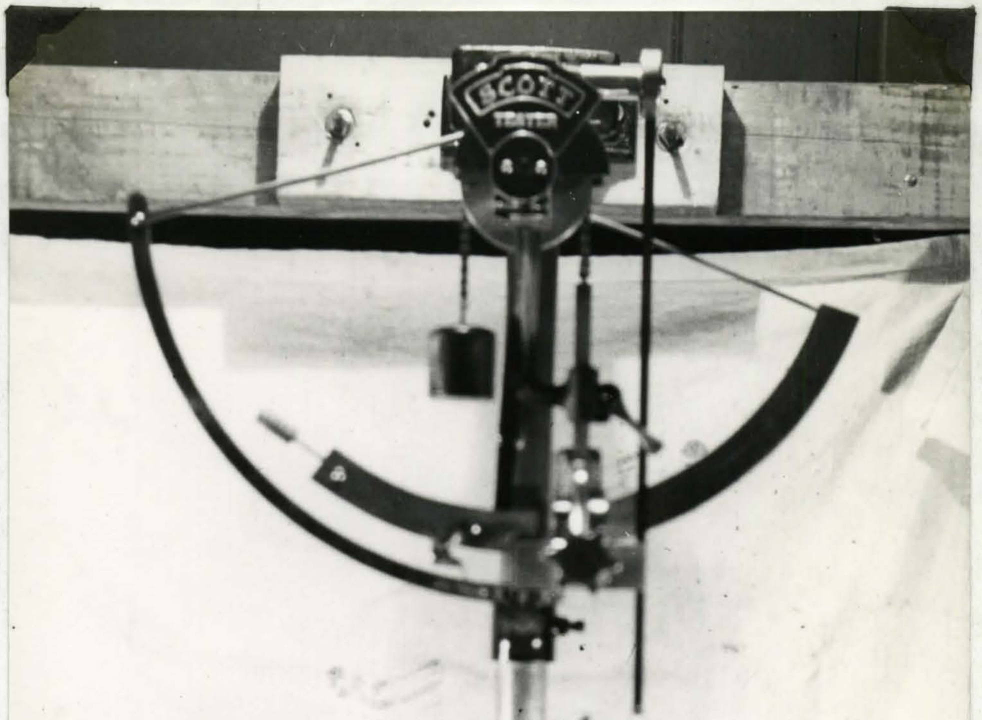

Fig. 4. Tensile Tester Used for Determining Per Cent Elongation of Films.

CONSTANT HUMIDITY CABINET.

The constant-temperature, constant-humidity cabinet (Fig. 5) consists of an insulated box maintained at a temperature of 70°F, and 50-54 per cent relative humidity. The temperature was controlled by a thermostatically operated heating unit of two 75-watt light bulbs, and a cooling coil through which cold water was circulated. The humidity was adjusted by means of a saturated solution of magnesium nitrate heptahydrate as suggested by Gardner (15).

EXTRACTION BATTERY.

The extraction of the varnish films was carried out in a battery of five units, each unit containing twelve Sohxlet extraction assemblies (Fig. 6). The units were constructed in the form of rectangular wooden boxes lined with asbestos paper, and fitted with removable lids in which were cut holes to receive the extraction flasks. Cylindrical metal reflectors were placed around the flasks to direct the heat from the light bulbs which formed the heating element. Cooling water for the Sohxlet condensers were supplied through an iron pipe manifold running the length of the unit.

Each Sohxlet extraction assembly consisted of a 400-ml. flask, a siphon cup, an extraction thimble, and a condenser cap. The siphon cup containing the extraction thimble was suspended by fine wires from the condenser cap which rested on the neck of the flask.

Fig. 6. Extraction Unit for Determining Polymer Content.

EXPERIMENTAL PROCEDURE

PREPARATION OF SAMPLES.

The varnishes included in this investigation were compounded from the materials selected by cooking each oil with each resin and thinning with the proper solvent. The 16 and 33 gallon oil length varnishes were cooked individually, and the 25 gallon oil length varnishes were prepared by blending these two lengths in the required proportions.

The cooking procedure for the different varnishes varied considerably because of the differences in the oil reactivities of the resins and the rates of bodying of the oils. In general, the procedure consisted in heating the oil or a combination of the oil and resin to a specified temperature, holding at this temperature for some time to increase the viscosity or "body" of the solution, and then adding more resin until all has been added and the desired "body" attained. The solution was then cooled to approximately 350°F, thinned with the required amount of solvent, and filtered.

A complete cooking schedule is given in Table II.

CASTING OF FILMS.

The films prepared for investigation were cast with a doctor blade on tin-coated panels placed upon a plate-glass surface. The doctor blade had a clearance of 0.008 inches, and the dried film was approximately 0.002 to 0.003 inches in thickness, the variation being attributable to the differences in the solid content and viscosities of the varnishes.

TABLE II

COOKING SCHEDULE FOR PREPARATION OF VARNISH SAMPLES

Sample	Proportion Resin Added Initially	Minutes to reach Temp.	Holding Temp.	Minutes Held at Temp.	Proportion Resin Added Secondarily	Minutes Held at Temp.	Proportion Resin Added Finally
LE1	0	45	590° F	40	1/2	100	1/2 *
LE3	¼	50	590° F	35	1/4	30	1/2*
LN1	0	35	600° F	35	1 *		
LN3	0	35	580° F	15	1 *		
LB1	1	35	550° F	30			
LB3	1	35	550° F	50			
TE1	½	45	580° F	110	½ *		
TE3	½	50	590° F	55	½ *		
TN1	0	30	580° F	10	1 *		
TN3	0	40	580° F	10	1 *		
TB1	1	40	500° F	30			
TB3	1	30	500° F	30			
DE1	0	45	580° F	20	½	65	1/2*
DE3	0	40	580° F	20	½	20	1/2*
DN1	0	45	580° F	15	1	15-460° F	
DN3	0	35	580° F	20	1	20-480° F	
DB1	1	40	520° F	10			
DB3	1	40	520° F	50			

Note: * Indicates that the mixture was heated to solution of the resin.

WEATHERING.

The films were allowed to dry in air for three days after casting. They were then placed in the accelerated weathering unit and exposed to the action of ultra-violet radiation, water spray, and refrigeration. The various weathering stages of the unit were united in different combinations to give a complete weathering action which attempted to approximate actual weathering conditions. A twenty-four hour cycle, based upon one developed by the Commonwealth Edison Company of Chicago, was adopted.

This cycle is given below:

Weathering Conditions	Cabinet Temperature	Time
Heat, light and water spray	40° C	4 hours
Heat and light	65° C	4½ hours
Heat, light and water spray	40° C	4 hours
Water spray	20° C	2 hours
Rest period	Room	6 hours
Refrigeration period	-20° C	1 hour
Examination of panels	Room	2½ hours

EXAMINATION OF PANELS.

After the refrigeration portion of the weathering cycle, the films were examined for cracking, peeling, checking and other types of failure.

STRIPPING AND HUMIDIFICATION OF FILMS.

After removal from the accelerated weathering unit, each panel was allowed to rest for one day prior to the stripping of the film. It was then inclined at an angle of approximately fifteen degrees with the horizontal, and a drop of mercury placed at the upper edge of the film. The panel remained in this position overnight, during which time the tin surface under the film was amalgamated with mercury. On the following day the edges of the film were trimmed with a razor blade and the film was lifted free of the panel. The film was then suspended in the constant-temperature, constant-humidity cabinet and left there for three days to reach equilibrium conditions.

DISTENSIBILITY TESTING.

Two strips measuring one by six inches were cut from each film after removal from the humidity cabinet. The strips were cut with a razor blade, using a flat steel bar as a pattern. The thickness of these strips was measured by means of a micrometer.

The sample strip was then clamped in the testing machine and a load applied. The elongation of the film and the load required to break it were recorded, and from these measurements the per cent elongation and the tensile strength of the film were determined.

EXTRACTION.

The polymer content of the aged film was determined by extracting the film with acetone and considering the insoluble portion as polymer.

A double thickness Whatman extraction thimble in which was folded a double thickness of #30 Whatman filter paper was extracted with acetone for one day, dried at 105-110° C, and weighed. The weighings were performed in a large weighing bottle on an analytical balance. The film sample was cut into small pieces and approximately one gram was placed in the thimble. The thimble was again dried, and weighed, the weight of the sample being obtained by difference. The thimble was then placed in the extraction battery, and extracted for approximately two weeks to constant weight. Two blank thimbles were extracted with each ten samples to minimize errors resulting from slight changes in the weight of the thimble itself. The loss in weight of the sample was obtained by difference, and the per cent of insoluble polymer remaining was calculated.

DATA AND RESULTS

Values for the per cent unextractable and the per cent elongation of the varnish films after successive periods of aging are shown in tables III-VI. The data from these tables are plotted in figure 7-38, the curves showing the relation between the per cent unextractable and the age in cycles, and the relation between the per cent unextractable and the per cent elongation of the film.

It was impossible because of mechanical difficulties to obtain distensibility measurements on films which were aged sufficiently to become brittle. Therefore, no values for per cent elongation were obtained less than 0.7. It is reasonable to assume in view of the trend of the other measurements, that the elongation of a film reduces to a very low value at high polymer content, and therefore, the curves plotting the per cent unextractable against the per cent elongation have been extrapolated to zero per cent elongation and one hundred per cent polymer content. The broken lines of the curves show the extrapolated data.

In aging the varnish films, the cycles at which visual failure occurred were noted. From the curves, figures 7-38, the values of the per cent unextractable at these cycles were approximately determined. These data are shown in Table VII.

TABLE III

PERCENT UNEXTRACTABLE IN AGED VARNISH FILMS

Sample	Age in Cycles					
	0	2	4	6	8	10
LE1	52.2	60.2	61.5	----	62.4	----
LE2	67.6	62.4	71.7	70.2	69.8	----
LE3	64.1	67.0	57.7	73.6	69.5	70.3
LN1	44.2	52.3	37.0	51.6	----	----
LN2	55.8	57.7	60.5	64.7	55.4	----
LN3	60.9	63.5	54.9	66.0	58.3	63.7
LB1	83.0	83.0	57.0	85.0	69.1	80.7
LB2	80.0	83.6	71.6	84.6	78.6	80.2
LB3	82.0	85.9	78.6	85.0	79.9	81.8
LA1	78.5	88.9	84.4	89.2	90.0	80.5
LA2	83.5	85.1	80.3	91.2	88.0	79.3
LA3	75.2	86.5	77.5	92.6	84.8	70.0
TE1	45.4	63.0	69.5	62.7	64.6	----
TE2	57.3	71.4	70.8	70.6	80.0	76.1
TE3	61.5	76.0	70.6	74.3	83.0	77.5
TN1	40.3	57.2	47.8	51.4	48.4	----
TN2	50.9	63.9	62.7	62.4	69.0	72.3
TN3	56.3	63.6	67.8	66.1	71.0	76.7
TB1	81.3	89.1	70.6	83.8	76.7	81.5
TB2	80.0	88.0	77.5	85.0	76.6	80.2
TB3	80.6	84.6	82.3	88.3	80.9	84.0
DE1	69.0	67.5	71.6	70.8	80.4	88.4
DE2	60.5	75.3	76.6	69.9	82.8	79.4
DE3	67.6	80.0	72.9	76.6	89.1	62.5
DN1	42.6	61.2	52.7	67.9	66.0	54.1
DN2	51.0	73.2	68.3	68.6	73.5	61.6
DN3	55.0	49.9	65.9	77.2	68.9	64.5
DB1	84.0	88.2	84.0	87.4	91.5	93.6
DB2	91.0	89.3	96.8	91.3	91.1	91.0
DB3	91.8	89.0	87.0	88.0	86.6	86.6
DA2	69.5	84.1	85.2	92.9	83.6	75.5
DA3	77.8	86.6	77.8	89.2	90.1	70.0

TABLE IV

CHECKS ON PERCENT UNEXTRACTABLE IN AGED VARNISH FILMS

Sample	Age in Cycles					
	0	2	4	6	8	10
LE1	47.0	66.9	----	61.5	----	----
LE2	54.1	69.5	----	----	----	----
LE3	59.1	73.5	73.8	69.0	71.2	77.3
LN1	47.7	61.4	55.4	----	51.8	----
LN2	45.5	64.5	68.0	57.8	62.1	71.3
LN3	64.0	67.9	69.9	66.0	66.3	71.2
LB1	81.8	80.0	84.2	76.6	73.8	83.1
LB2	79.1	84.4	83.6	81.0	81.7	84.1
LB3	82.5	87.6	84.7	84.0	82.0	88.5
LA1	----	----	90.6	----	----	89.5
LA2	91.3	----	90.6	85.7	----	82.5
LA3	----	----	91.1	84.6	82.5	88.6
TE1	----	----	61.9	----	----	----
TE2	----	----	----	----	69.9	----
TE3	----	76.5	----	----	72.1	----
TN1	----	55.2	----	----	----	----
TN2	----	----	----	61.5	----	----
TN3	----	----	----	61.0	----	----
TB1	75.0	77.4	80.1	77.5	82.3	83.2
TB2	80.4	83.0	85.6	83.4	85.0	87.0
TB3	82.2	85.6	----	83.5	87.5	----
DE1	69.8	----	----	73.8	69.0	75.6
DE2	----	----	----	76.0	72.6	----
DE3	74.5	74.7	80.2	73.4	75.2	83.2
DN1	----	----	59.9	----	----	63.3
DN2	----	77.6	----	----	66.3	71.5
DN3	----	81.0	----	64.0	77.5	71.3
DB1	90.2	91.6	85.9	----	----	----
DB2	92.7	87.6	----	----	----	----
DB3	91.2	87.7	91.5	----	----	----
DA2	----	----	----	83.4	77.8	70.0
DA3	----	----	76.8	----	----	78.0

TABLE V

PERCENT ELONGATION OF AGED VARNISH FILMS

Sample	Age in Cycles					
	0	2	4	6	8	10
LE1	****	----	----	---		
LE2	2.3	0.7	---	---	---	
LE3	54.4	1.3	0.7	2.6	---	---
LN1	****	0.7	---	---		
LN2	9.5	1.3	1.0	1.5		
LN3	55.3	4.7	1.3	1.6	2.0	---
LB1	****	---	---	1.7	---	1.2
LB2	98.0	6.5	4.2	4.2	2.1	4.1
LB3	84.2	11.7	8.7	4.3	3.5	2.6
LA1	99.5	8.6	6.2	3.5	5.7	3.2
LA2	57.0	46.1	59.9	32.1	12.5	2.0
LA3	43.3	67.1	72.1	38.3	29.3	6.5
TE1	****	----	---	---	---	
TE2	25.6	0.8	1.2	0.7	0.3	---
TE3	56.0	2.5	1.8	0.7	1.3	---
TN1	****	1.2	2.7	---		
TN2	29.1	1.7	1.7	1.6	1.2	---
TN3	62.6	2.4	1.7	1.7	1.8	1.2
TB1	****	1.3	---	1.5	1.0	1.6
TB2	41.1	4.5	3.5	4.2	2.5	2.7
TB3	66.5	7.6	5.5	2.2	3.2	5.1
DE1	****	1.6	1.6	---		
DE2	99.7	3.2	2.5	2.1	1.2	---
DE3	95.0	9.1	4.1	2.8	1.5	1.6
DN1	89.8	1.6	2.7	0.8	---	---
DN2	96.6	5.4	3.0	1.6	2.4	2.0
DN3	83.7	33.6	33.5	2.4	4.7	1.8
DB1	****	3.0	3.6	4.0	3.4	2.2
DB2	92.0	13.8	4.6	9.4	6.3	2.5
DB3	74.0	17.5	6.9	9.7	6.0	4.2
DA2	62.0	71.9	68.5	45.8	7.2	3.1
DA3	****	68.9	69.3	47.6	15.3	3.6

*** Indicates that the film was too plastic to pull.

--- Indicates that the film was too brittle to pull or was cracked.

TABLE VI

CHECKS ON ELONGATION OF AGED VARNISH FILMS

Sample	Age in Cycles					
	0	2	4	6	8	10
LE1	****	----		---		
LE2	5.2					
LE3	99.0		2.5	---	1.0	1.0
LN1	****		---		---	
LN2	86.0		1.3		1.4	---
LN3	73.4	3.1	9.3	---	2.1	---
LB1	****	----	7.9	---	---	---
LB2	97.5	4.2	---	5.3	6.9	2.7
LB3	99.5	5.4	10.5	17.7	7.5	3.4
LA1			56.2			6.7
LA2	59.6		65.8	56.4		9.4
LA3			41.0	48.9	44.2	17.7
TE1			---			
TE2					---	
TE3		5.1			1.3	
TN1		---				
TN2				1.8		
TN3				6.1		
TB1	****	---	---	2.7	1.8	1.3
TB2	58.6	6.7	10.1	5.5		2.8
TB3	73.8	23.1		6.0	6.2	
DE1	7.2			1.0	1.2	
DE2				3.6	2.5	
DE3	97.0	15.5	47.4	19.4	3.4	1.8
DN1			2.4			---
DN2		----			8.1	1.8
DN3		61.9		31.7		5.6
DB1	12.8	4.9	6.3			
DB2	98.8	22.0				
DB3	69.1	34.1	42.0			
DA2				49.7	51.4	26.7
SA3			57.8			31.9

**** Indicates that the film was too plastic to pull.

---- Indicates that the film was too brittle to pull.

TABLE VII

PERCENT UNEXTRACTABLE IN VARNISH FILMS AT FAILURE

Sample	% Unextractable
LE1	61
LE2	69
LE3	70
LN1	52
LN2	62
LN3	68
LB1	85
LB2	85
LB3	88
LA1	91
LA2	91
LA3	93
TE1	63
TE2	72
TE3	77
TB1	83
TB2	87
TB3	86
TN1	51
TN2	68
TN3	75
DE1	75
DE2	80
DE3	82
DN1	66
DN2	74
DN3	72
DB1	92
DB2	91
DB3	88
DA2	85
DA3	91

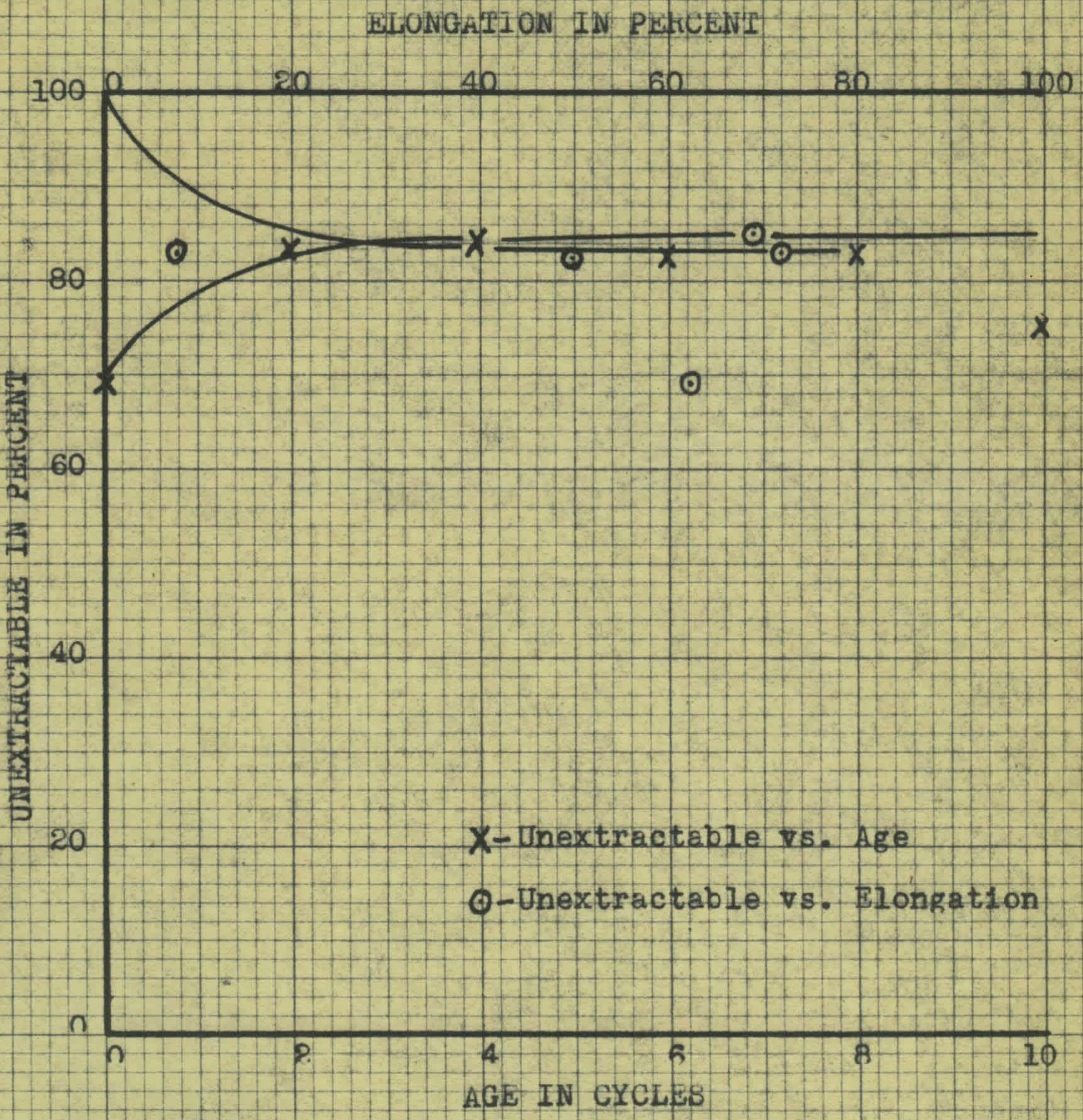

FIG. 7. PERCENT UNEXTRACTABLE VS. AGE AND ELONGATION FOR 25 GALLON CASTOR OIL*GLYCEROL PHTHALATE VARNISH.

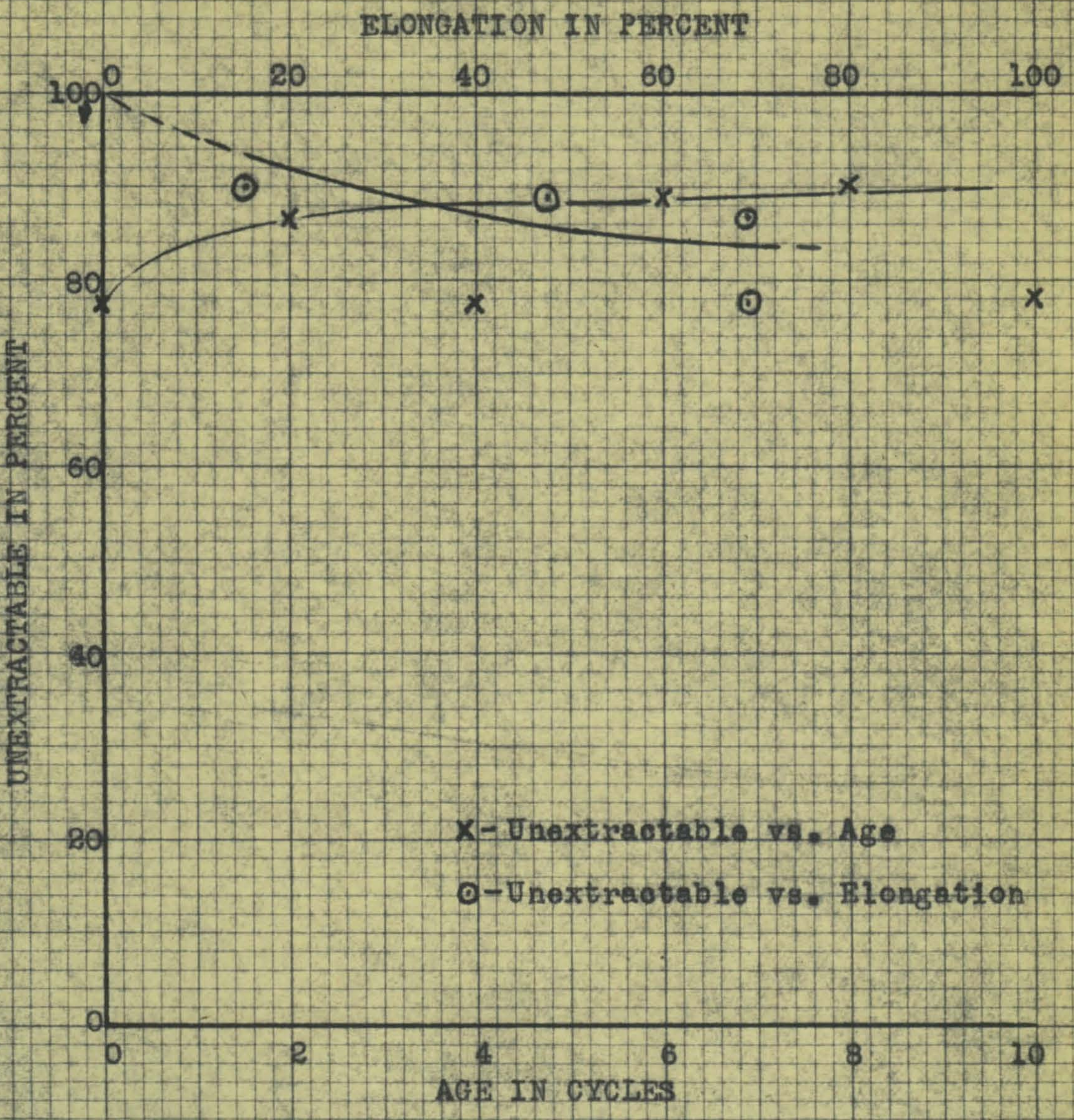

FIG. 8. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON CASTOR OIL-GLYCEROL PHTHALATE VARNISH.

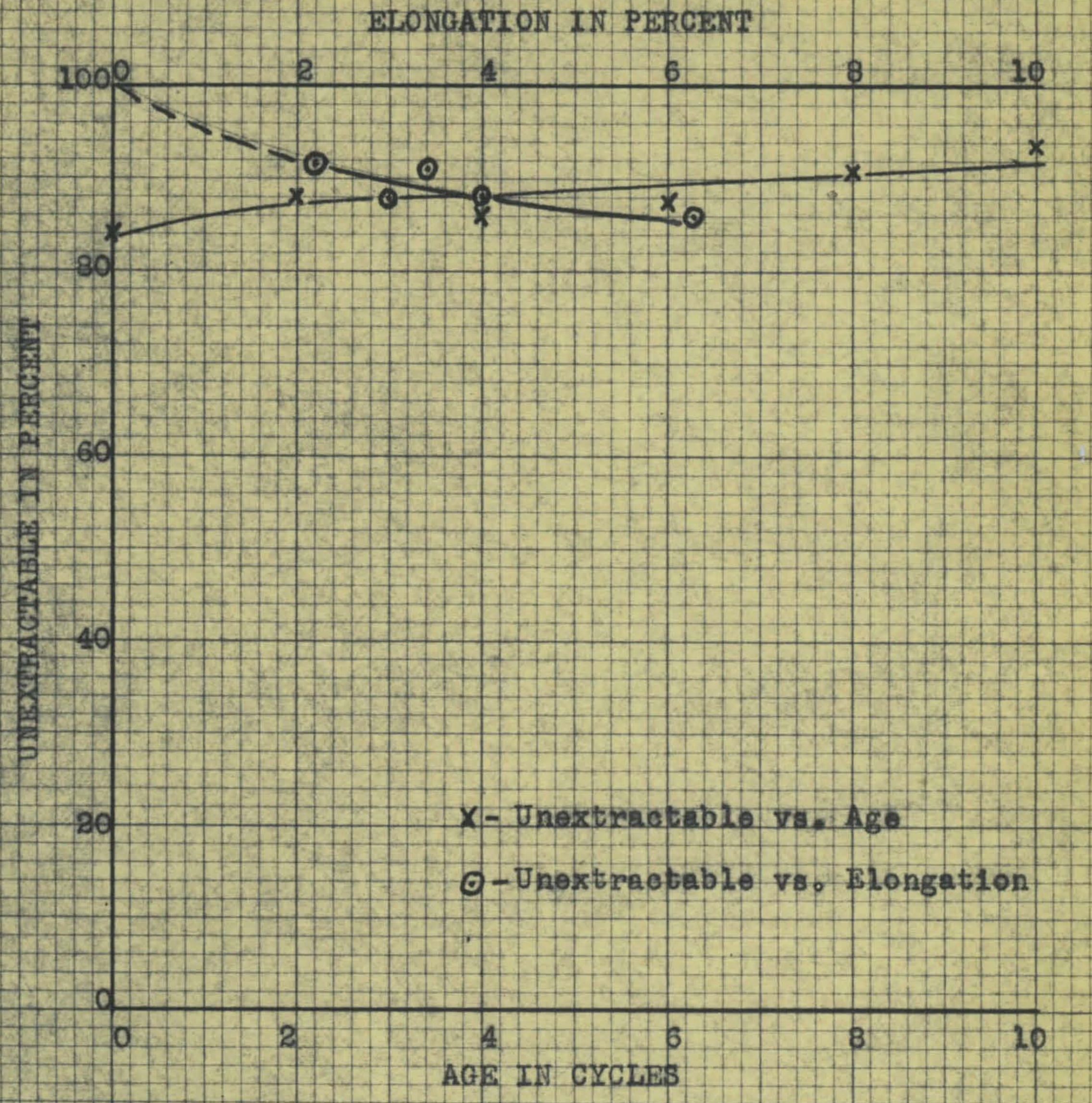

FIG. 9. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 16 GALLON CASTOR OIL-BAKELITE VARNISH.

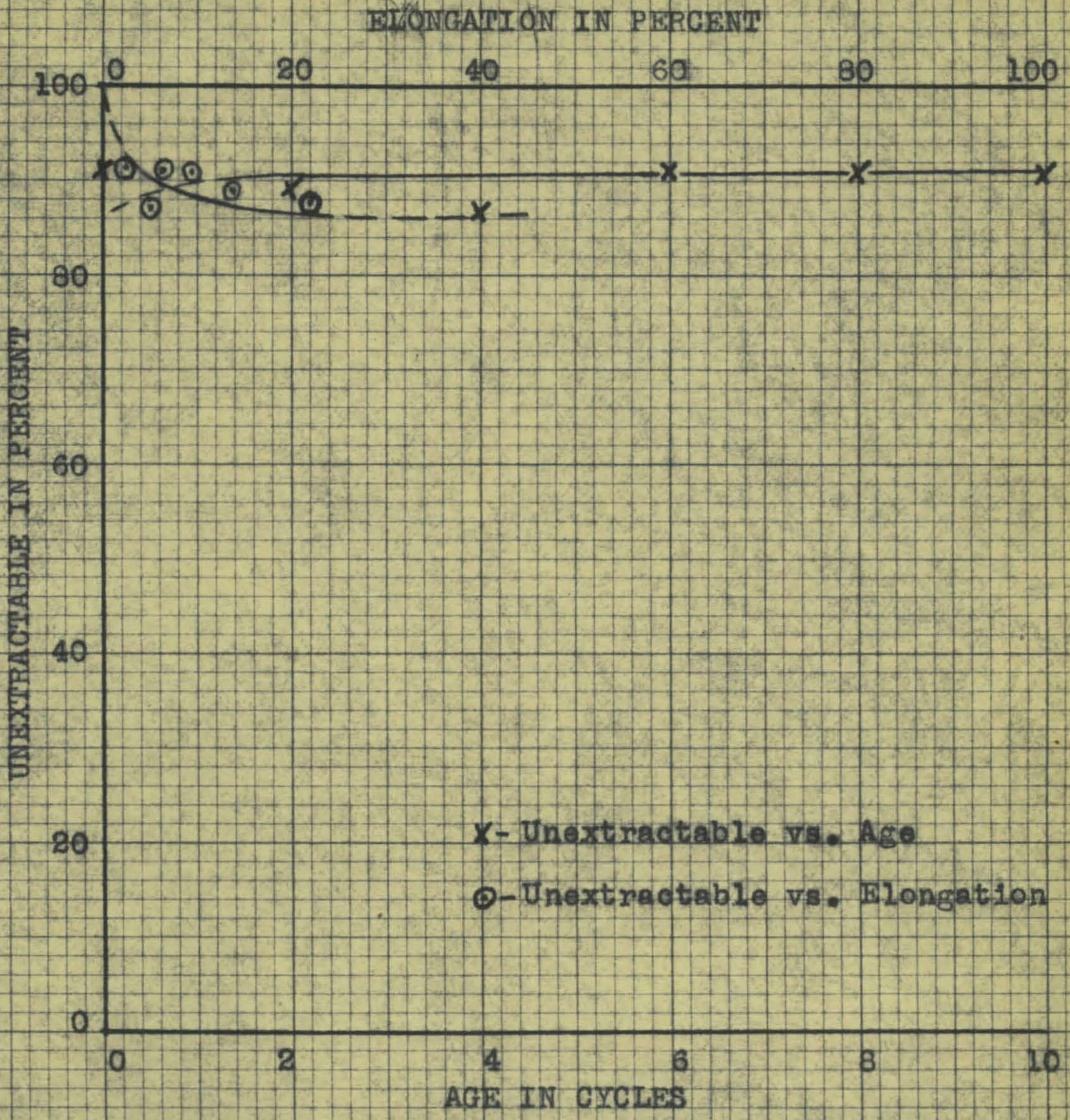

FIG. 10. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON CASTOR OIL-BAKELITE VARNISH.

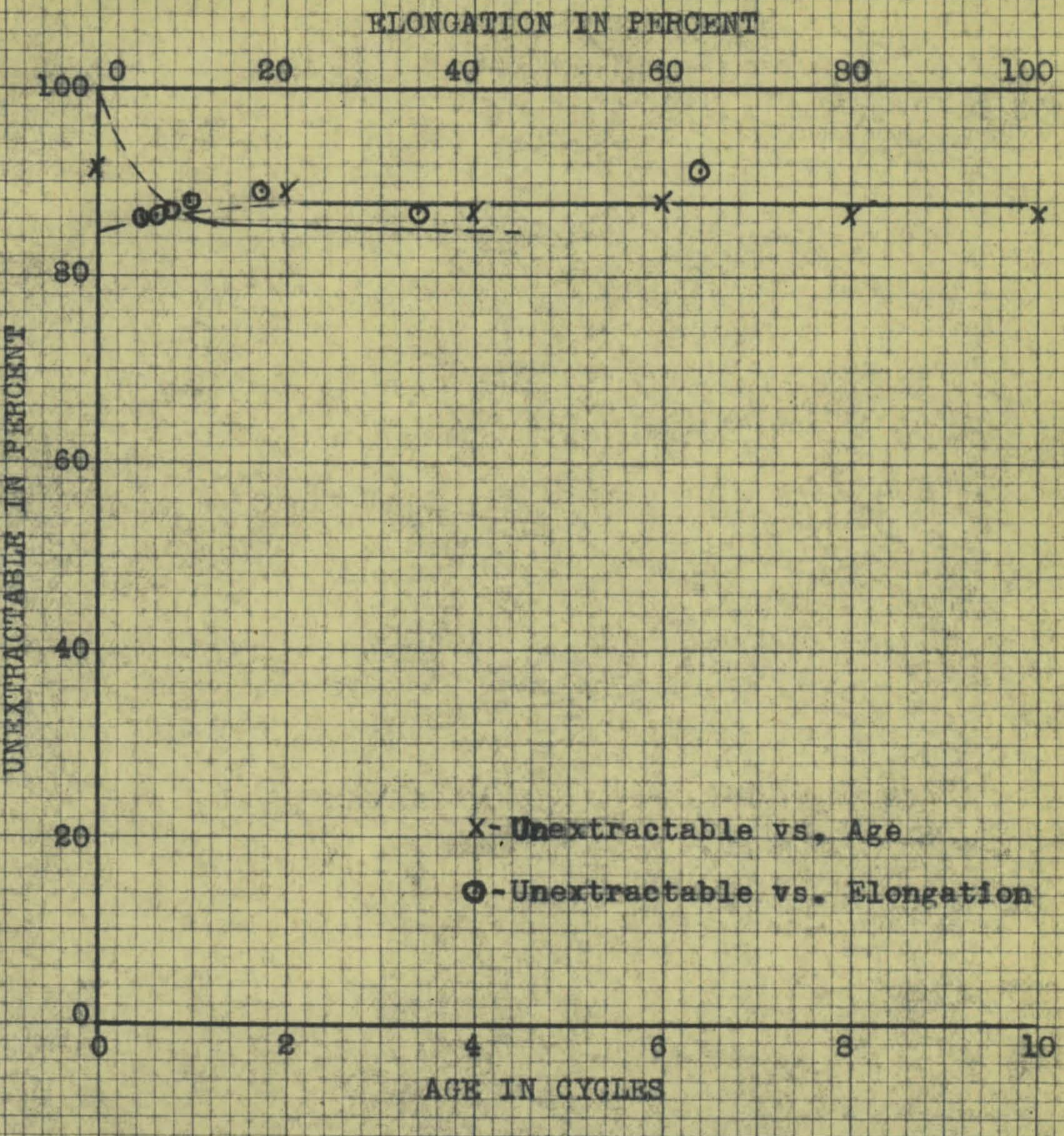

FIG. 11. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON CASTOR OIL-BAKELITE VARNISH.

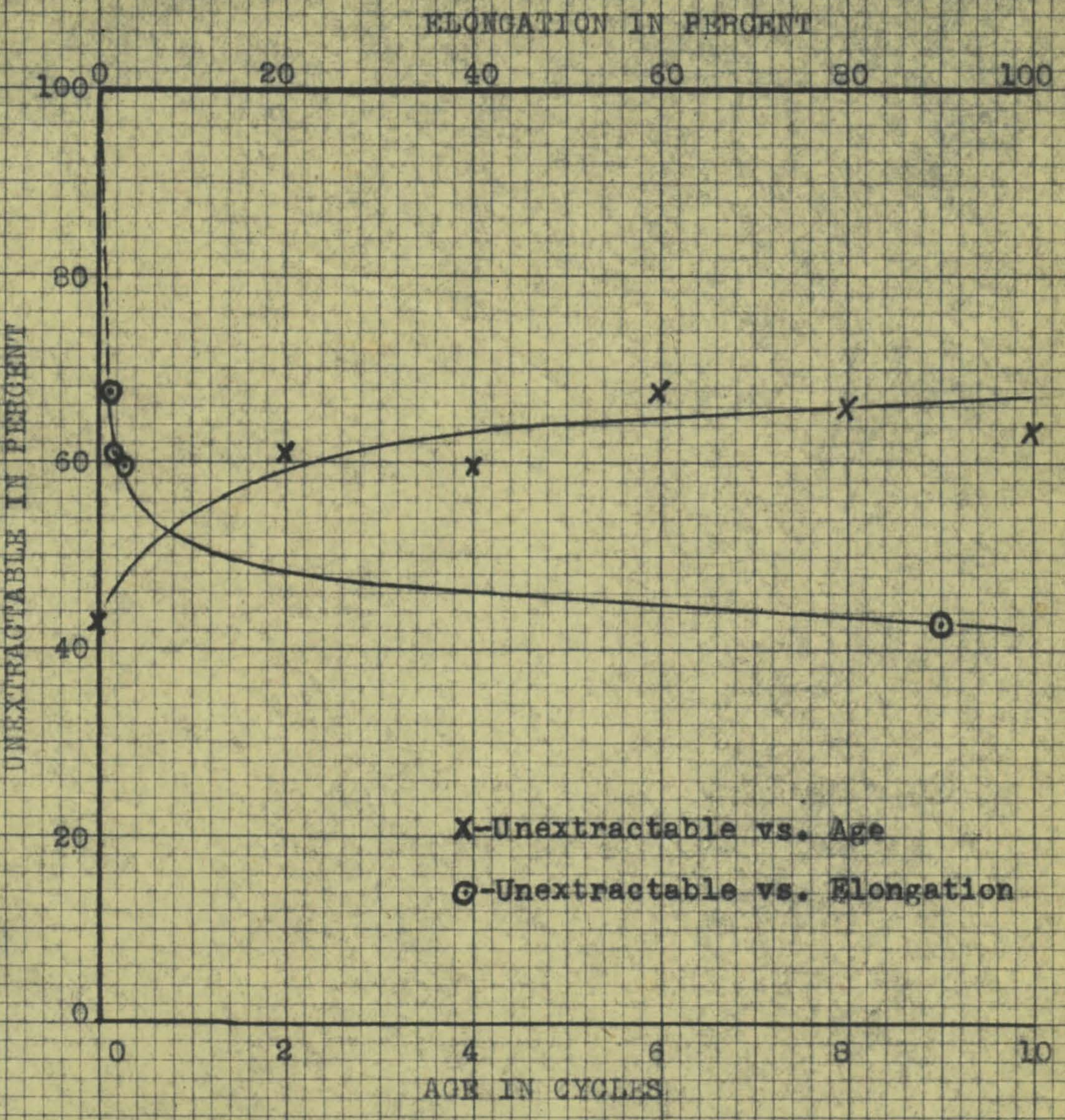

FIG. 12. UNEXTRACTABLE vs. AGE AND ELONGATION FOR 16 GALLON CASTOR OIL-NEVILLITE VARNISH.

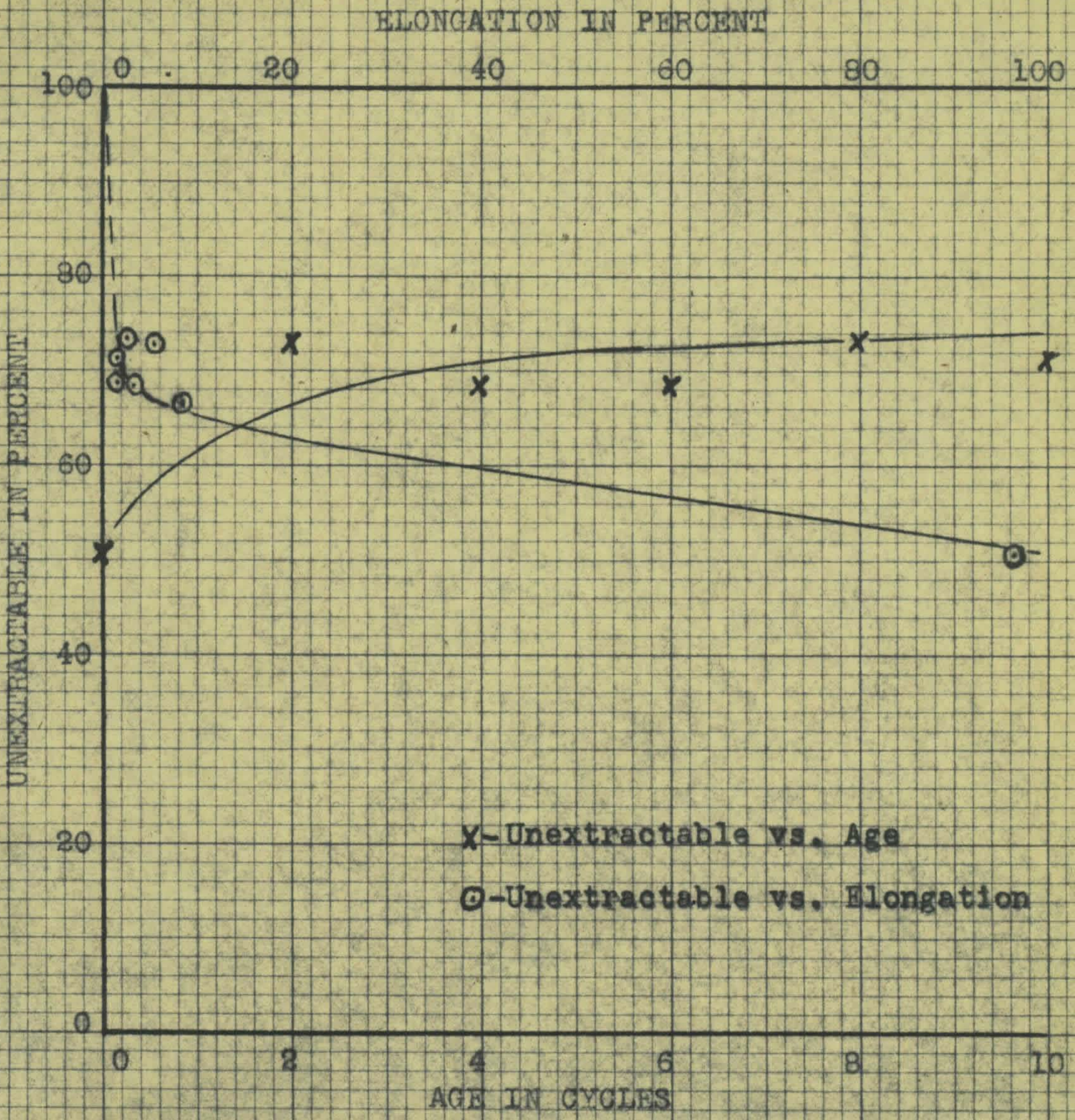

FIG. 13. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON CASTOR OIL-NEVILLITE VARNISH.

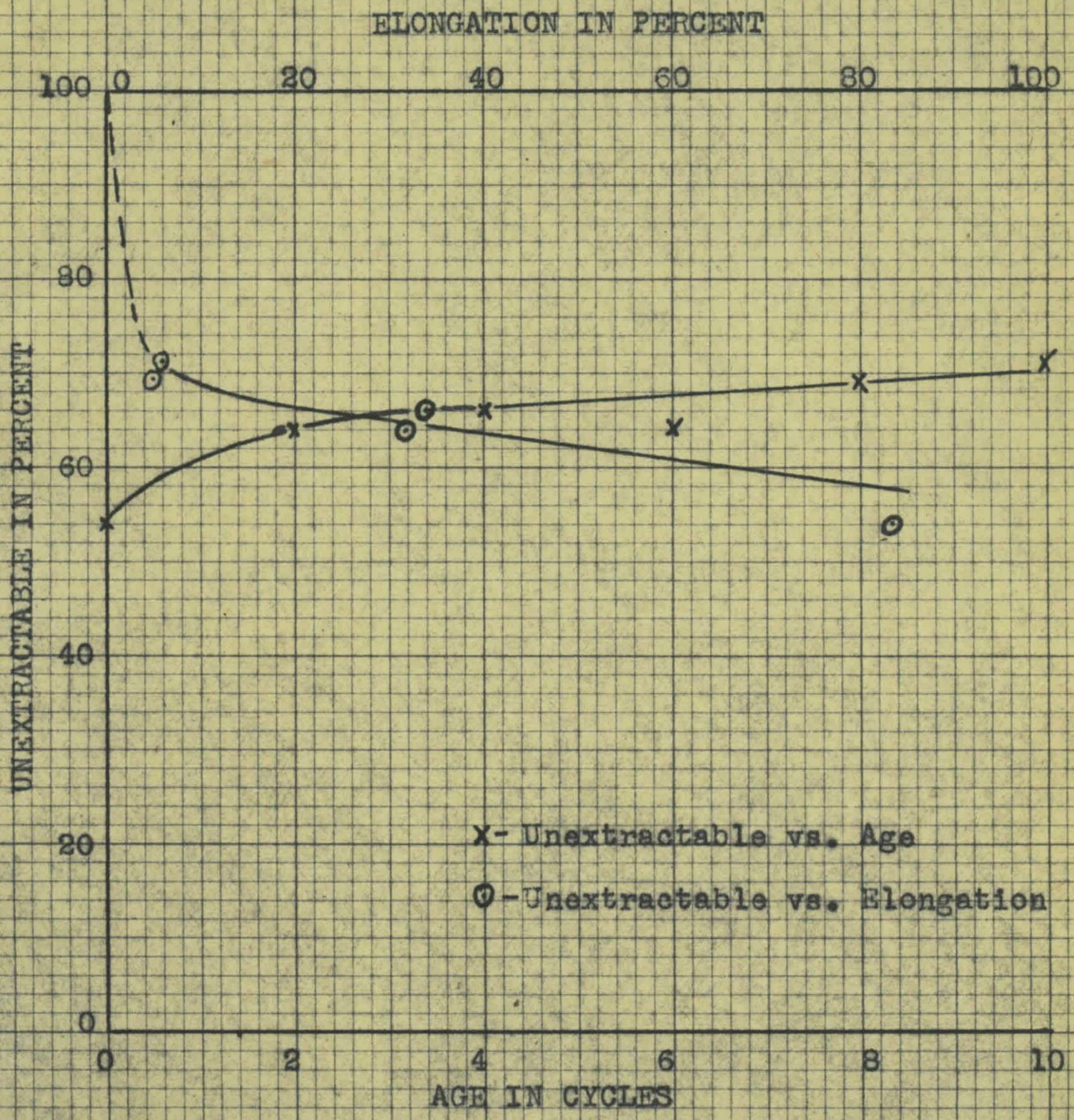

FIG. 14. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON CASTOR OIL-NEVILLITE VARNISH.

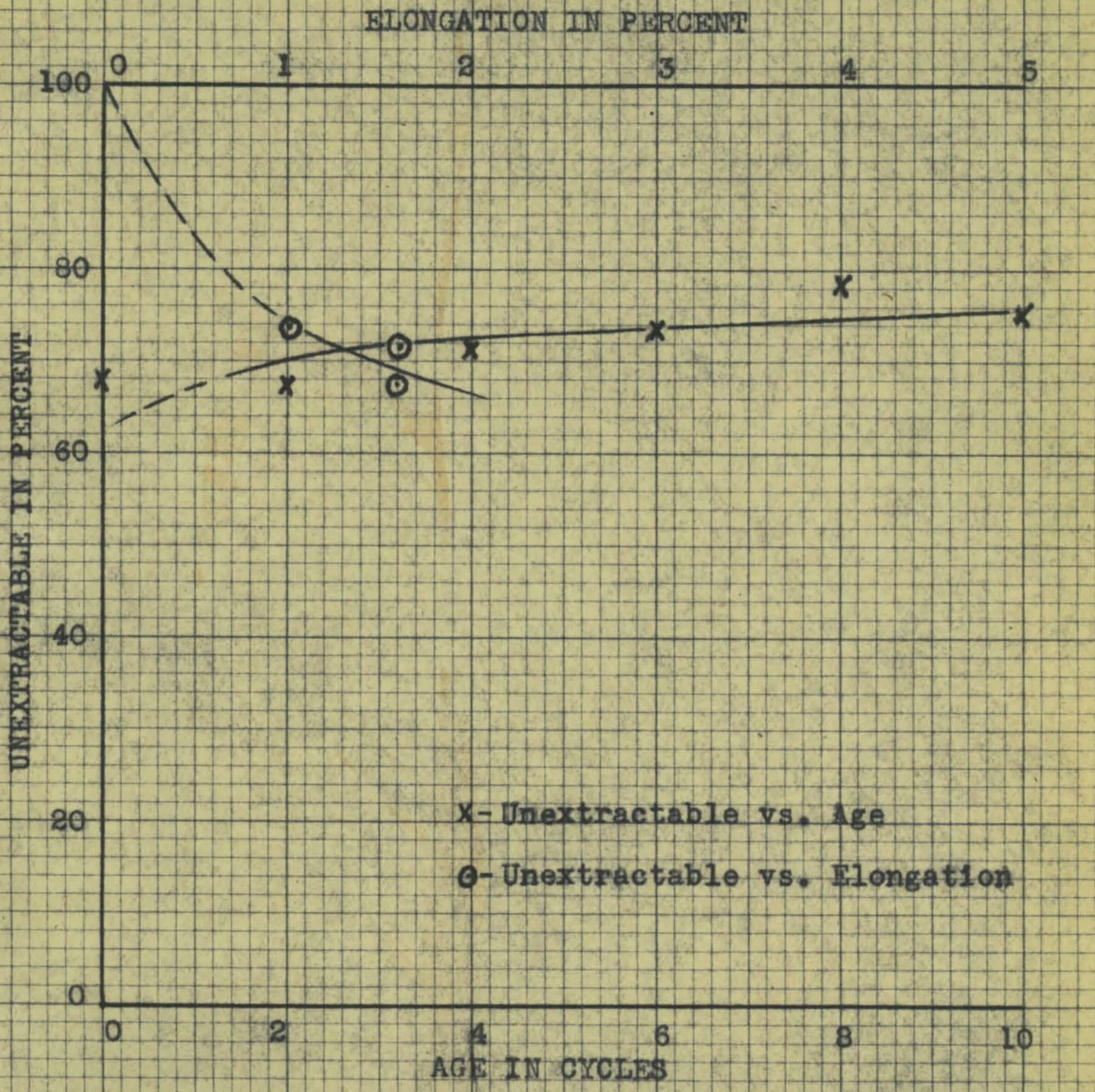

FIG. 15. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 16 GALLON CASTOR OIL-ESTER GUM VARNISH.

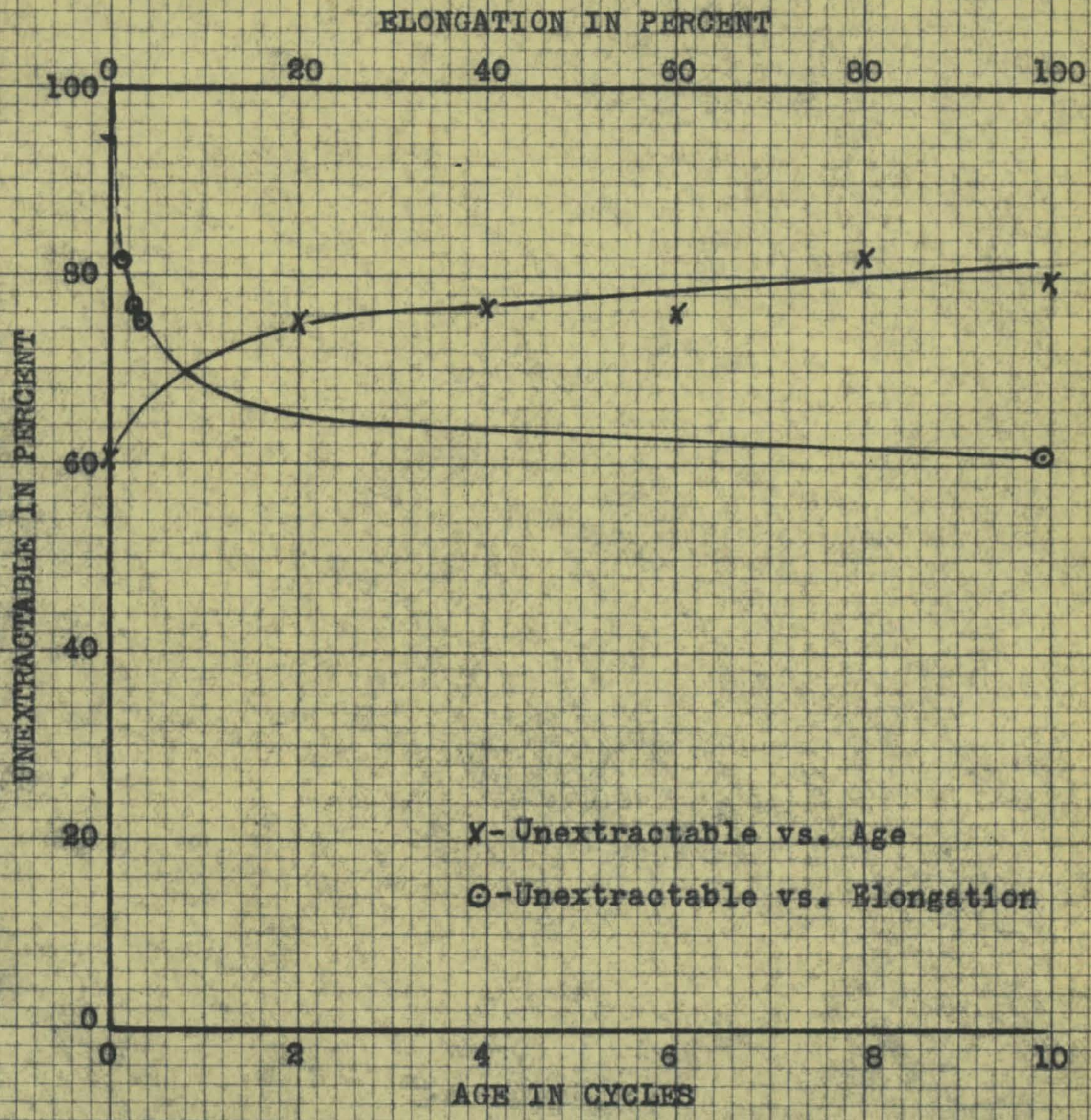

FIG. 16. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON CASTOR OIL-ESTER GUM VARNISH.

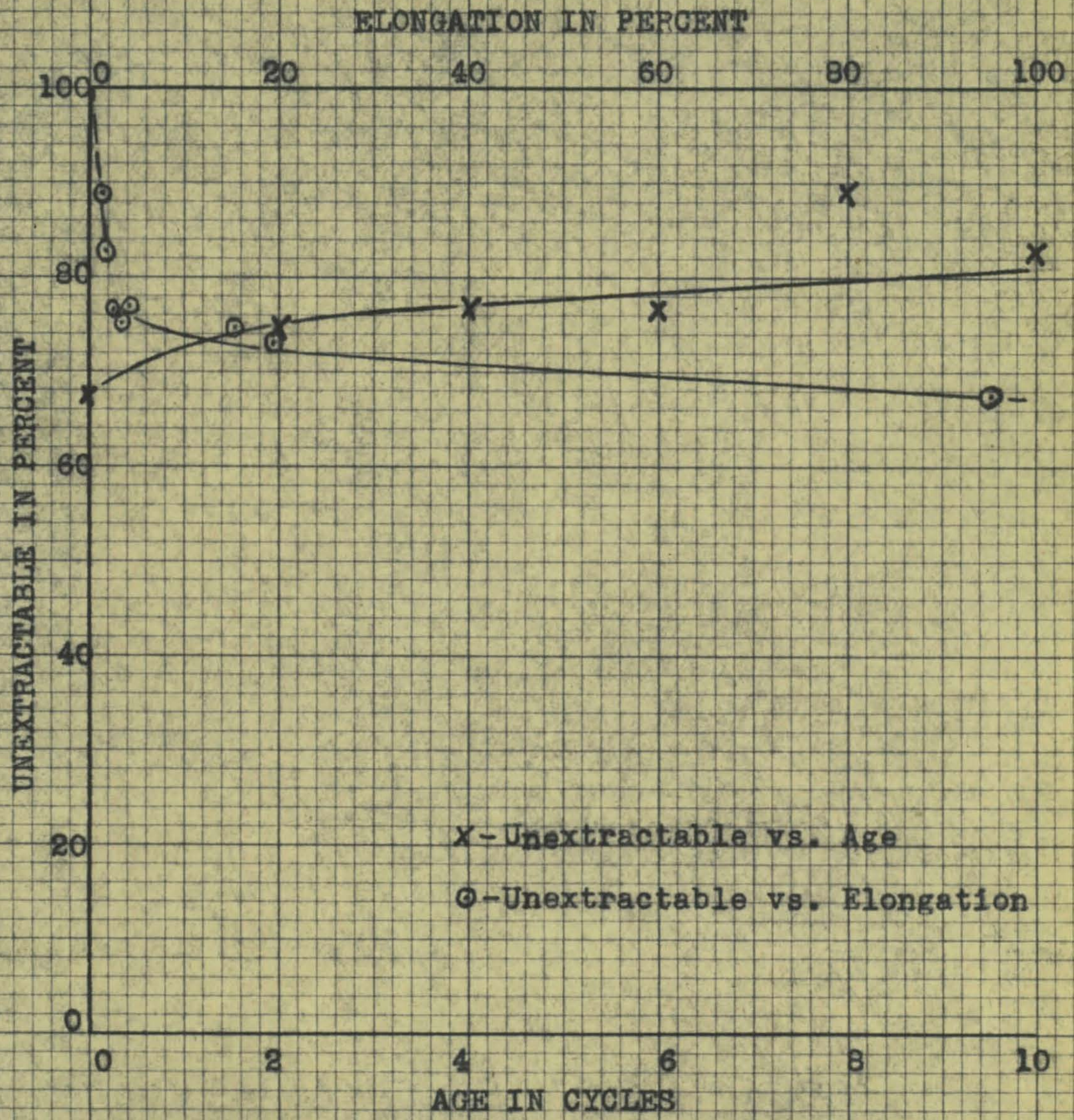

FIG. 17. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON CASTOR OIL-ESTER GUM VARNISH.

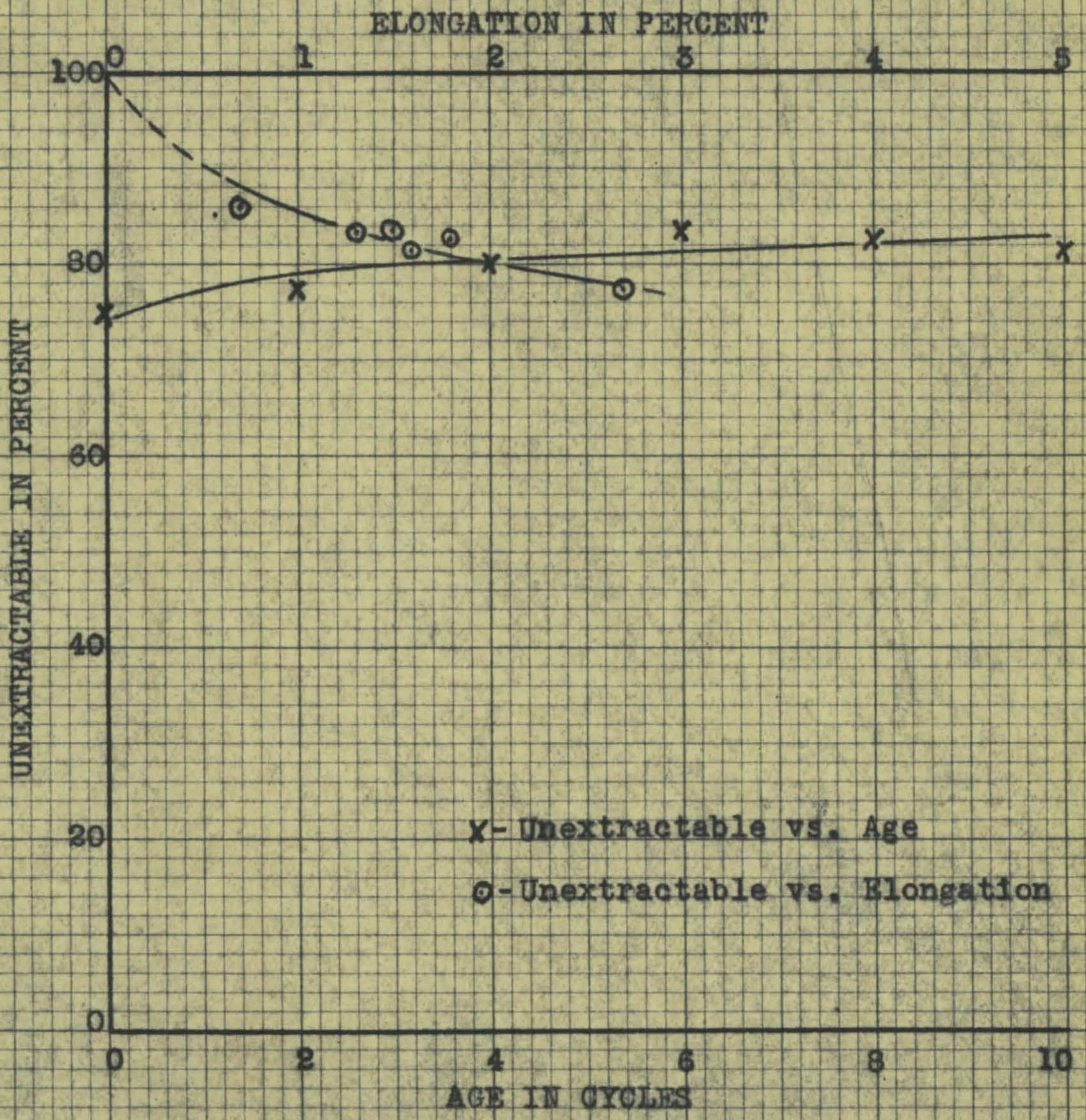

FIG. 18. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 16 GALLON CHINAWOOD-BAKELITE VARNISH.

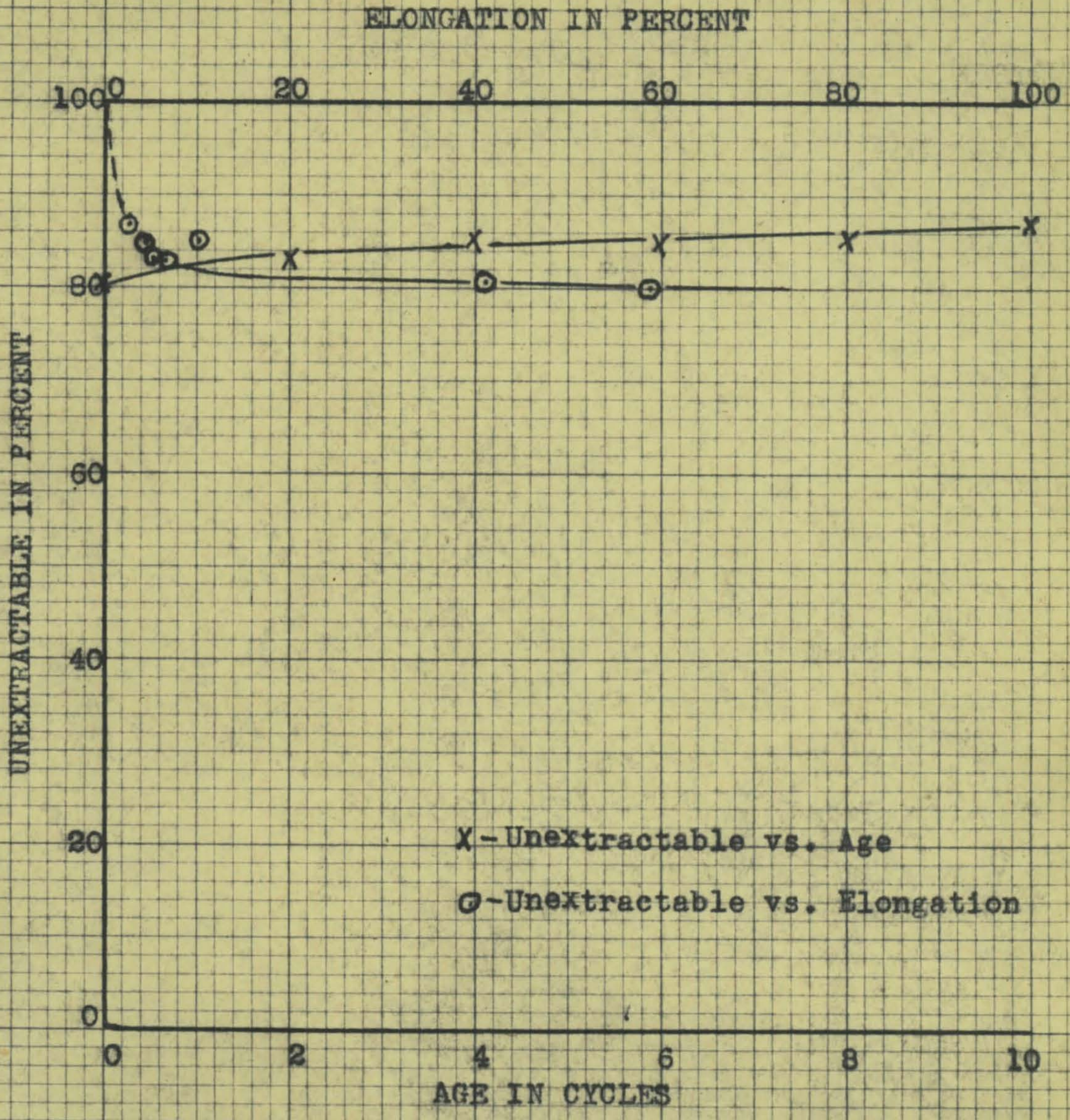

FIG. 19. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON CHINAWOOD-BAKELITE VARNISH.

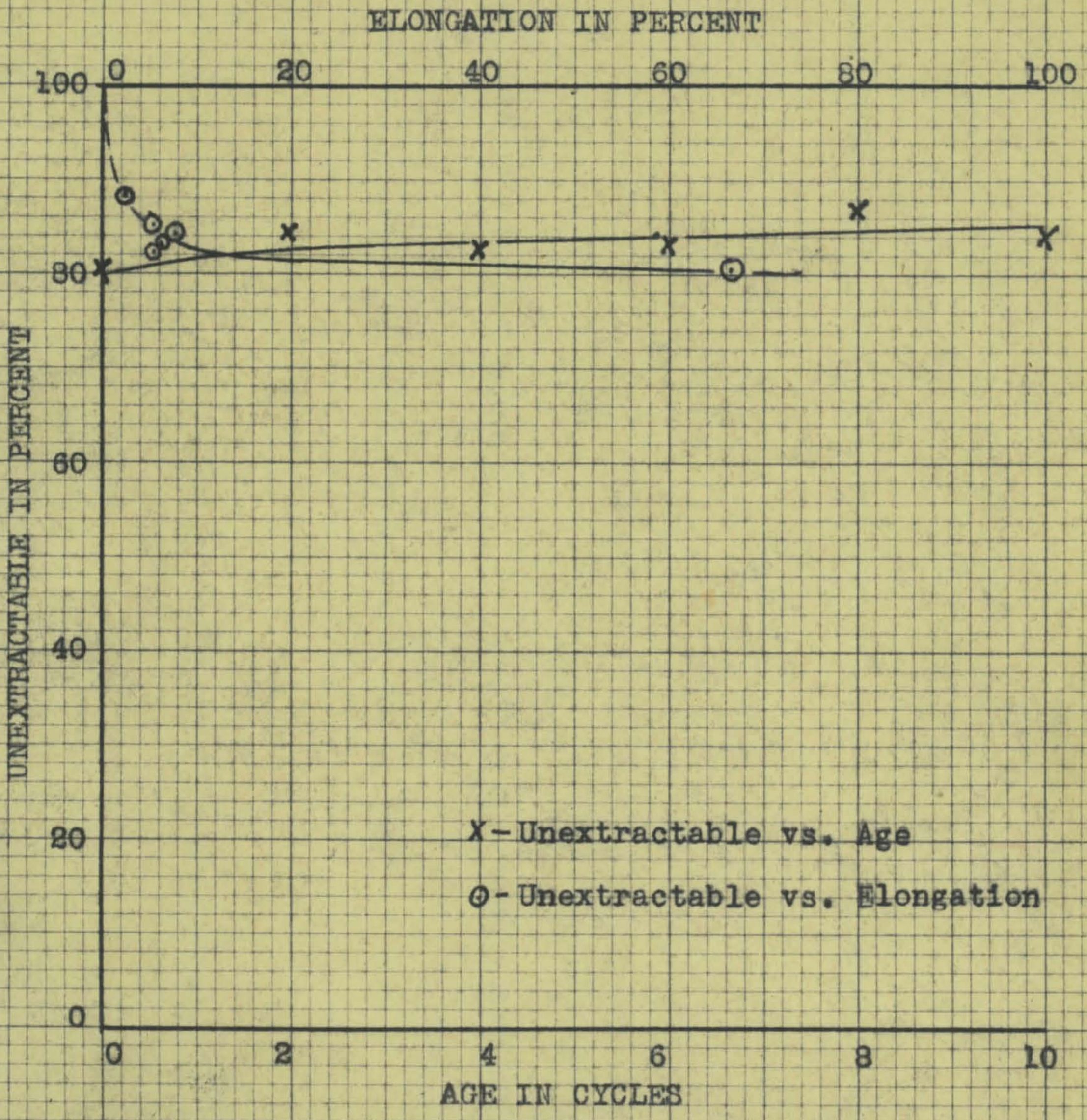

FIG. 20. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON CHINAWOOD-BAKELITE VARNISH.

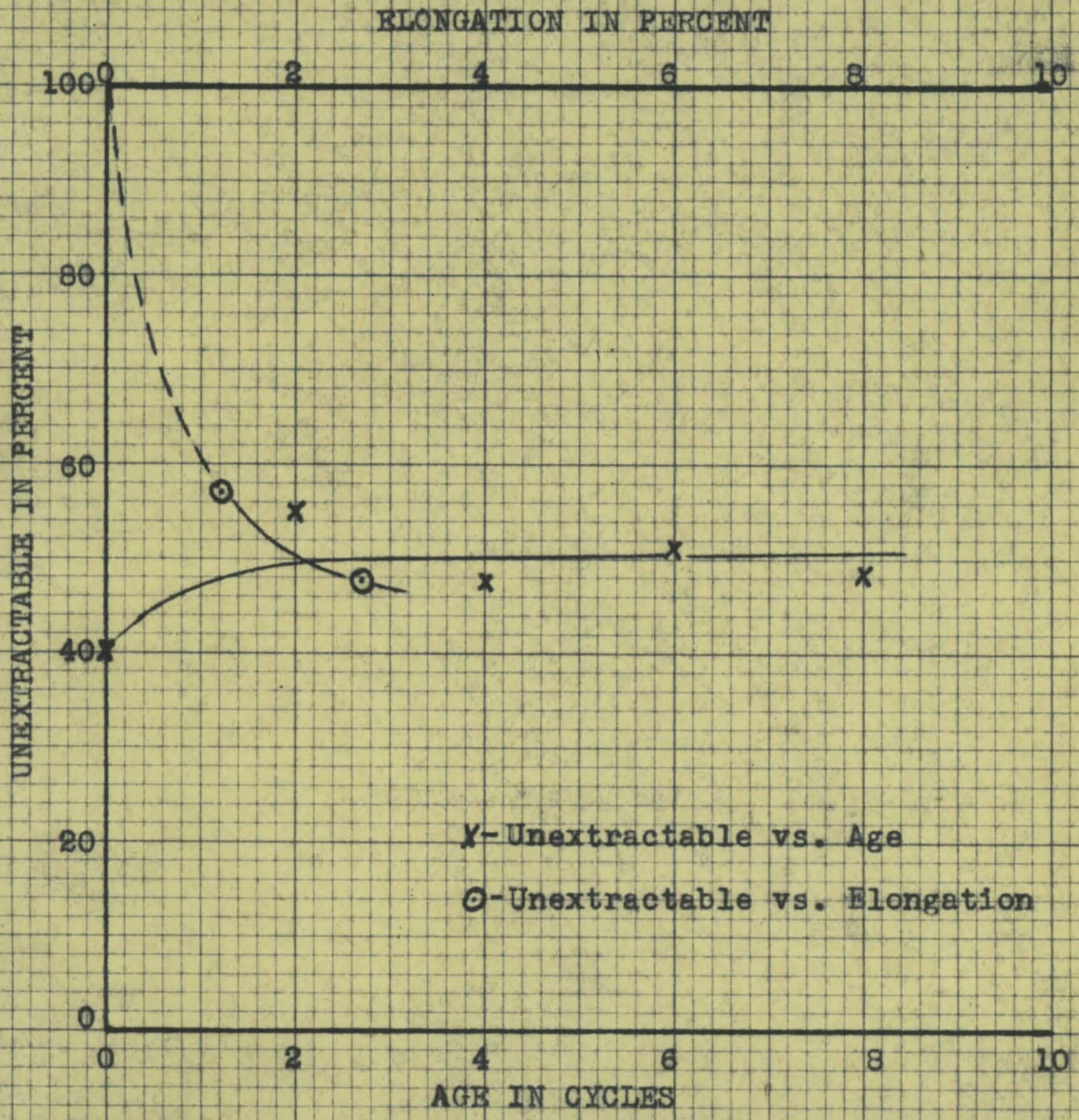

FIG. 21. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 16 GALLON CHINAWOOD-NEVILLITE VARNISH.

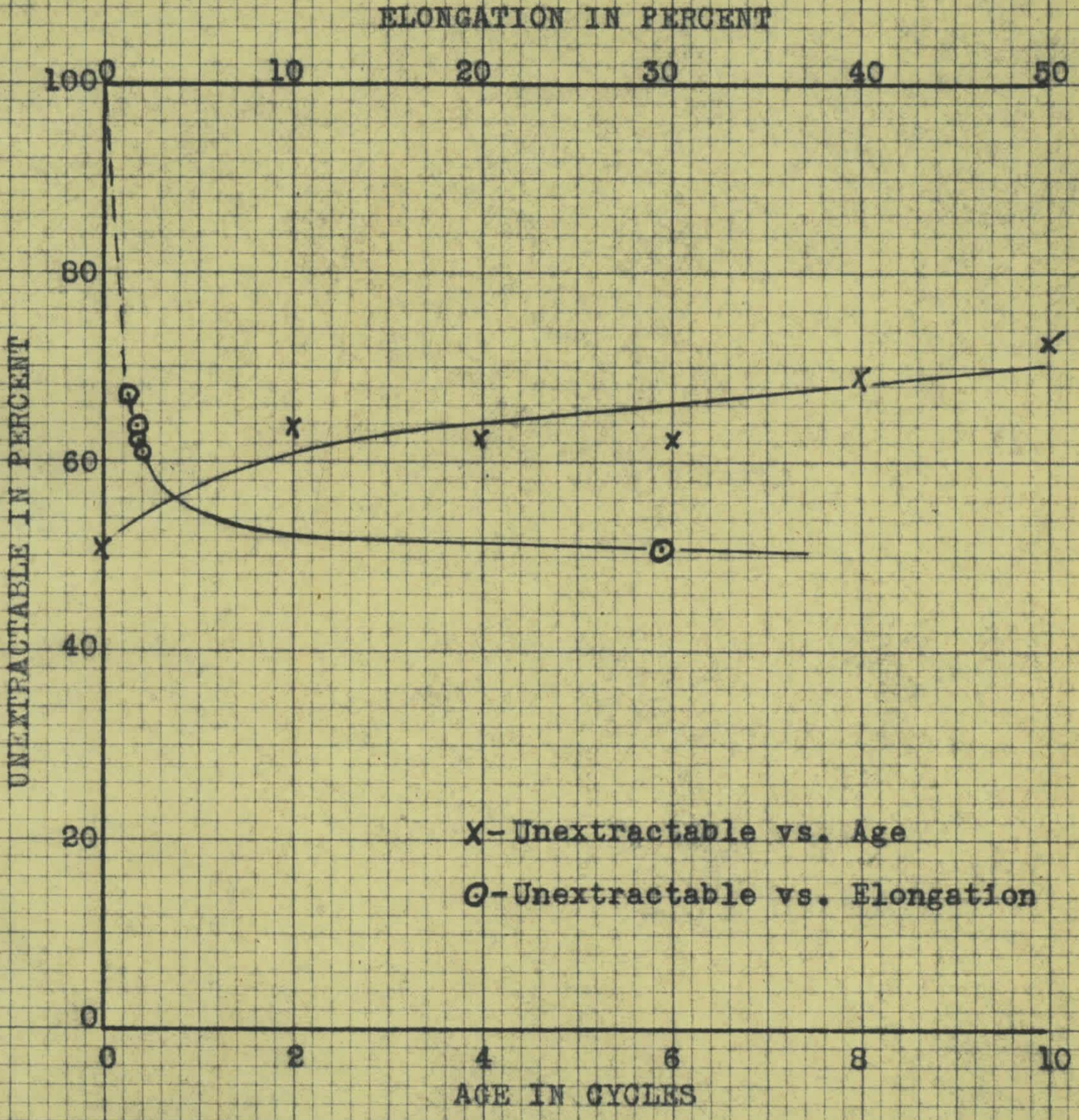

FIG. 22. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON CHINAWOOD-NEVILLITE VARNISH.

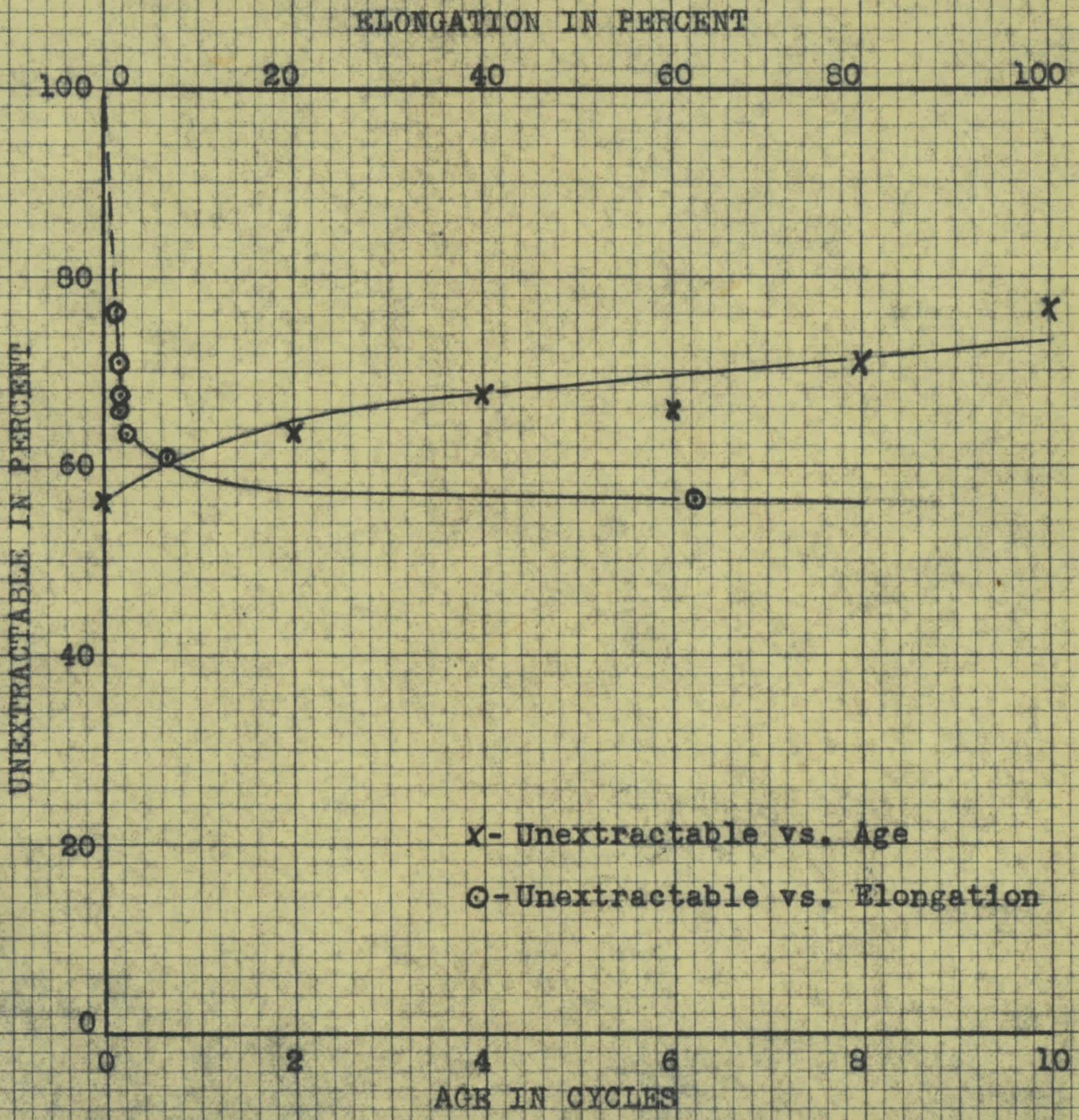

FIG. 23. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON CHINAWOOD-NEVILLITE VARNISH.

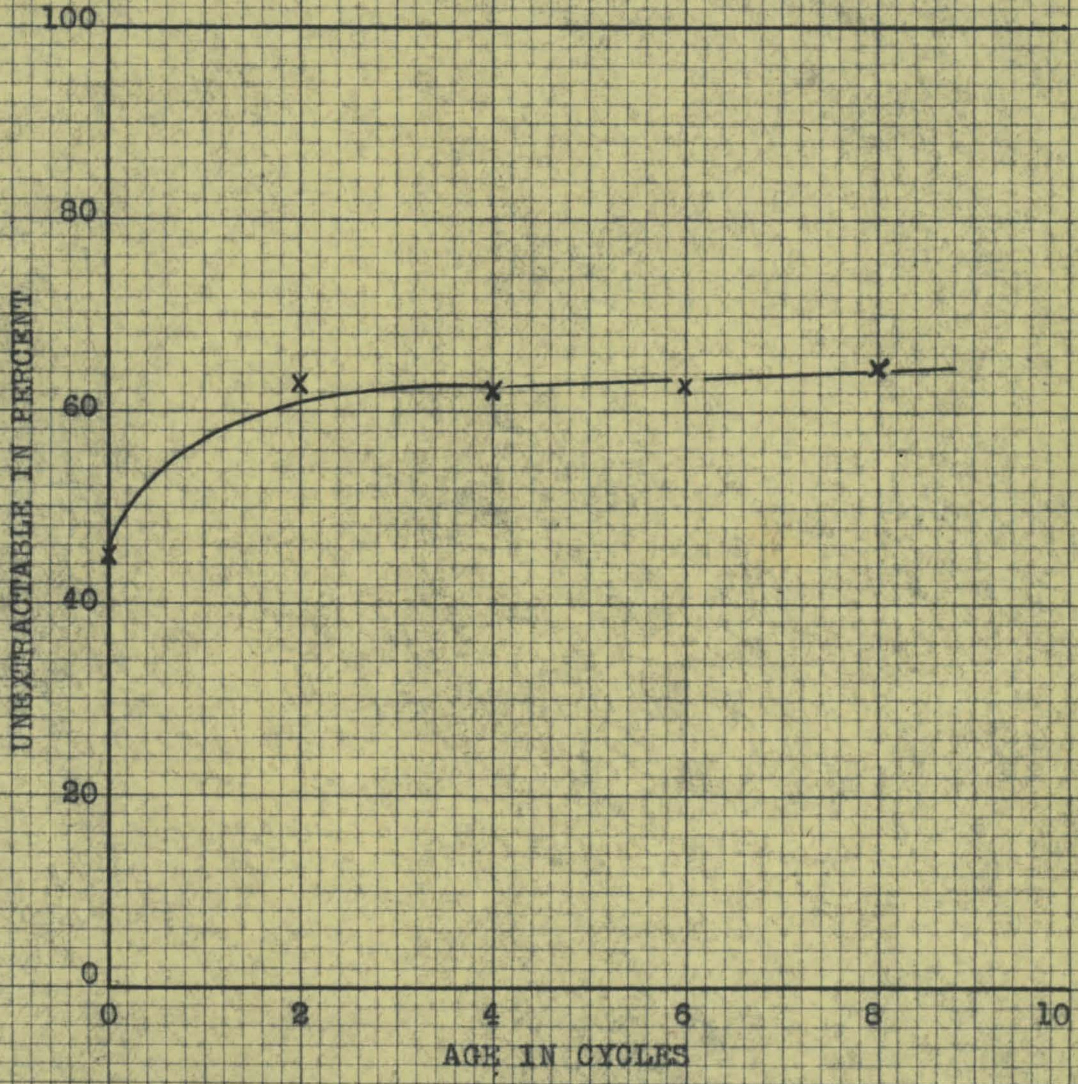

FIG. 24. PERCENT UNEXTRACTABLE vs. AGE FOR 16 GALLON CHINAWOOD-ESTER GUM VARNISH.

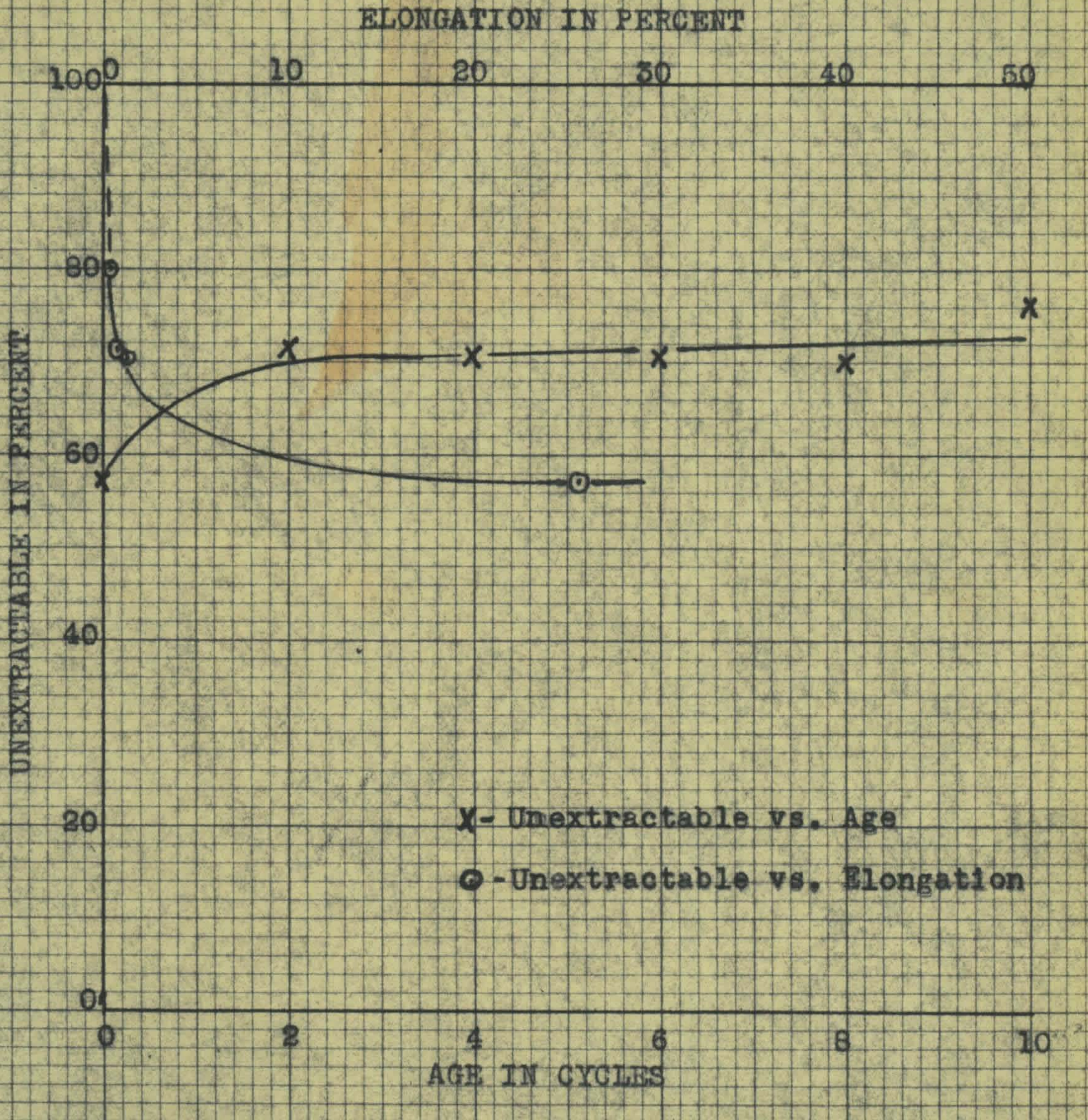

FIG. 25. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON CHINAWOOD-ESTER GUM VARNISH.

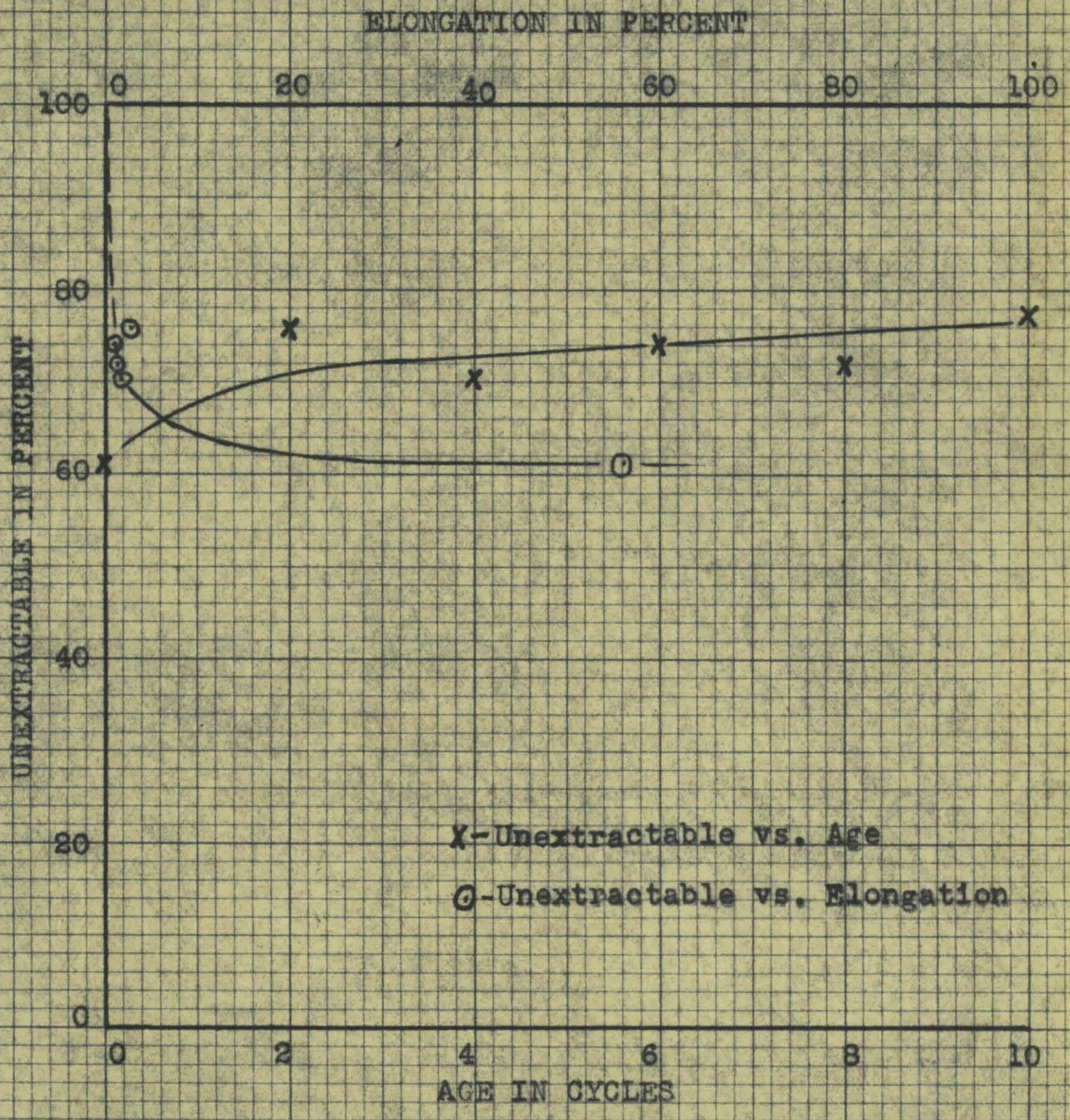

FIG. 26. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON CHINAWOOD-ESTER GUM VARNISH.

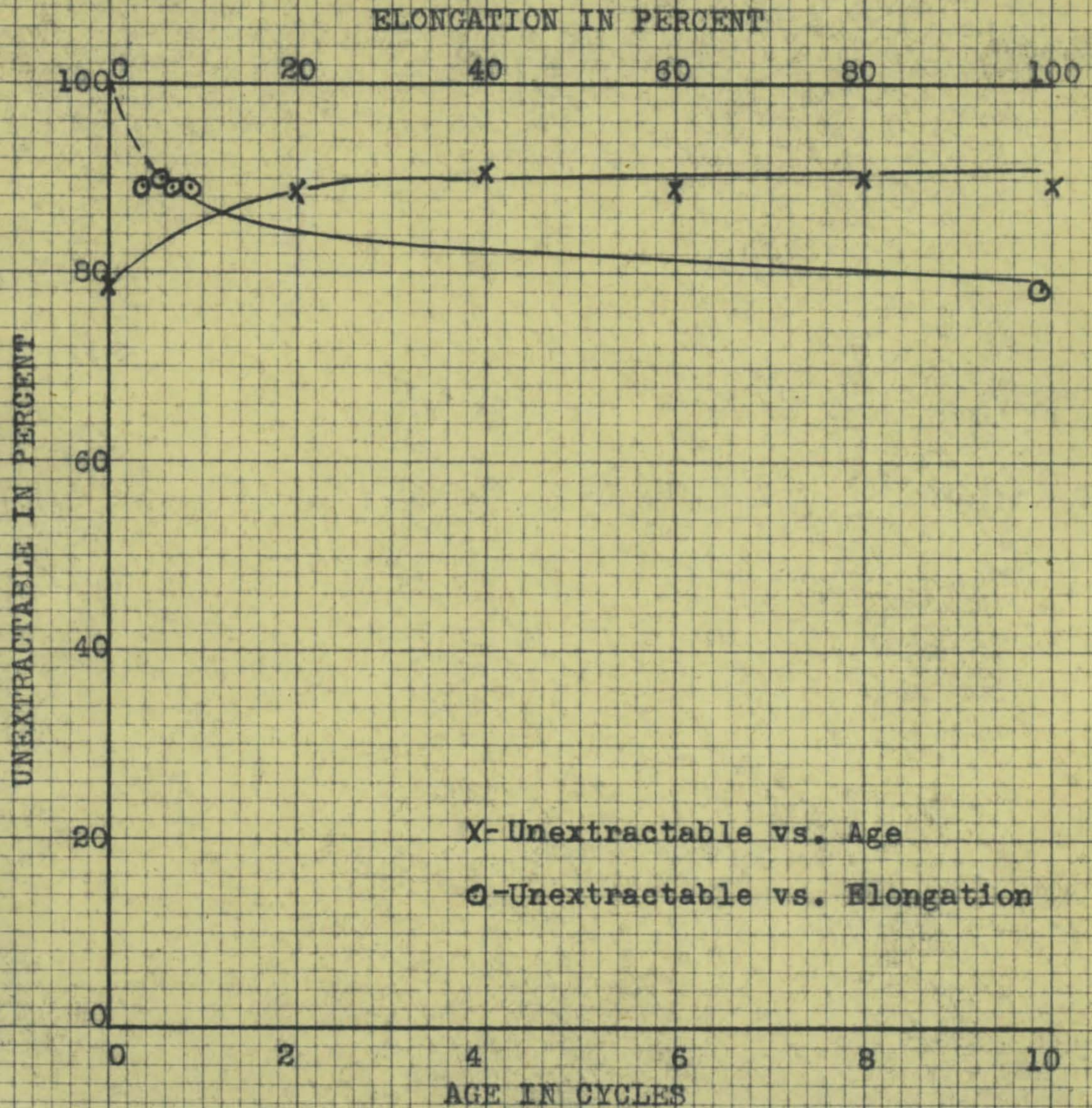

FIG. 27. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 16 GALLON LINSEED OIL-GLYCEROL PHTHALATE VARNISH.

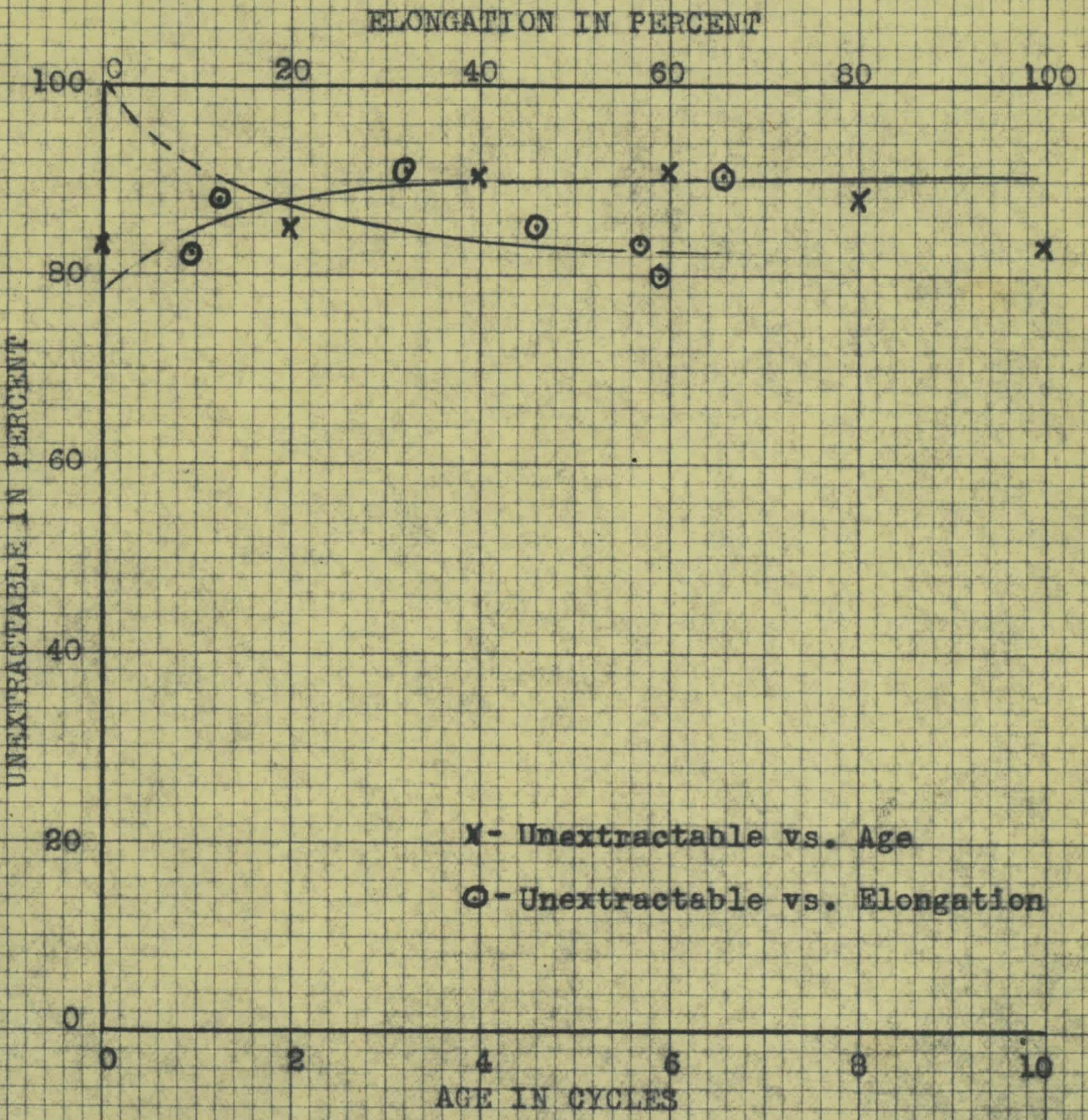

FIG. 28. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON LINSEED OIL-GLYCEROL PHTHALATE VARNISH.

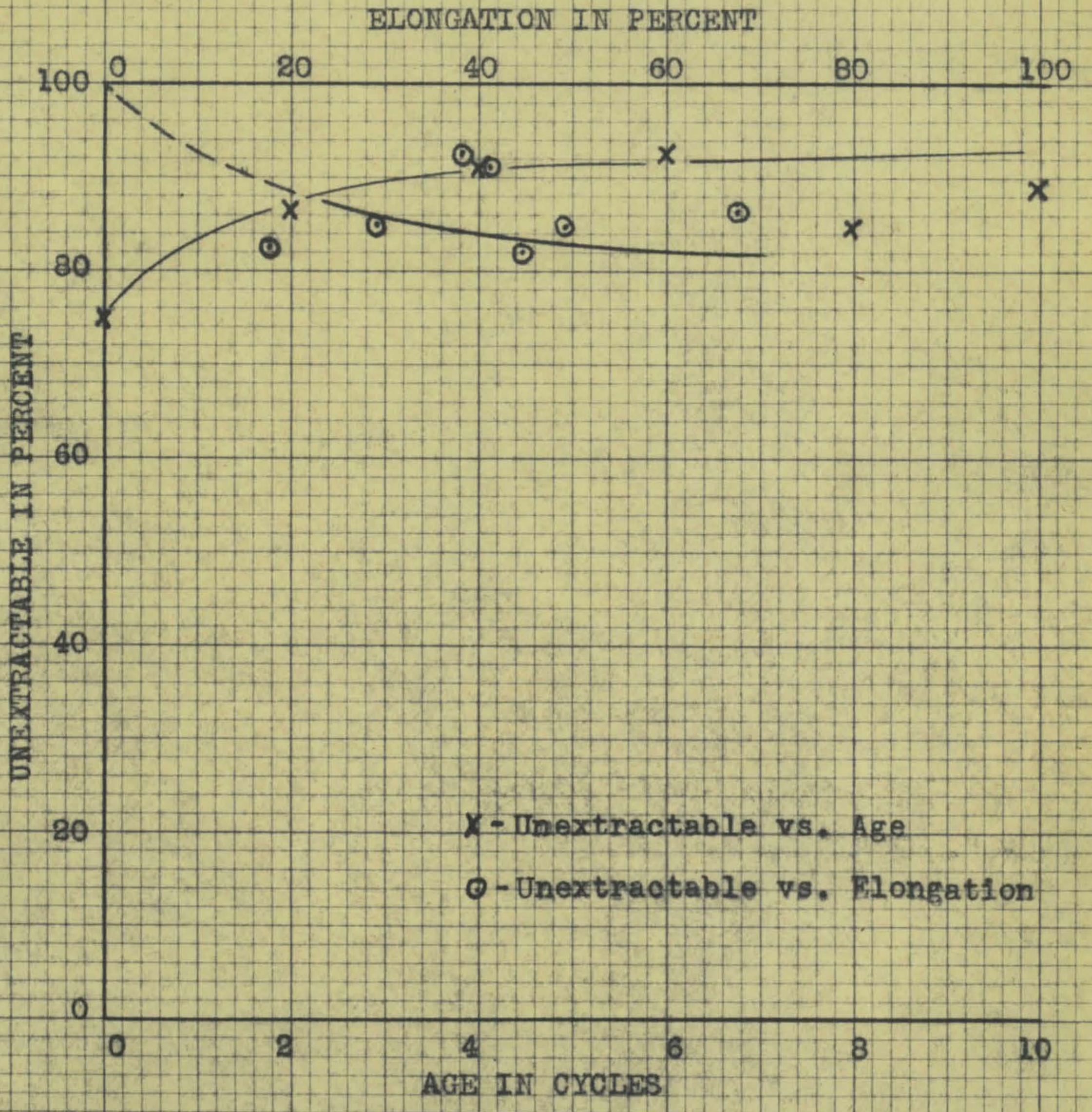

FIG. 29. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON LINSEED OIL-GLYCEROL PHTHALATE VARNISH.

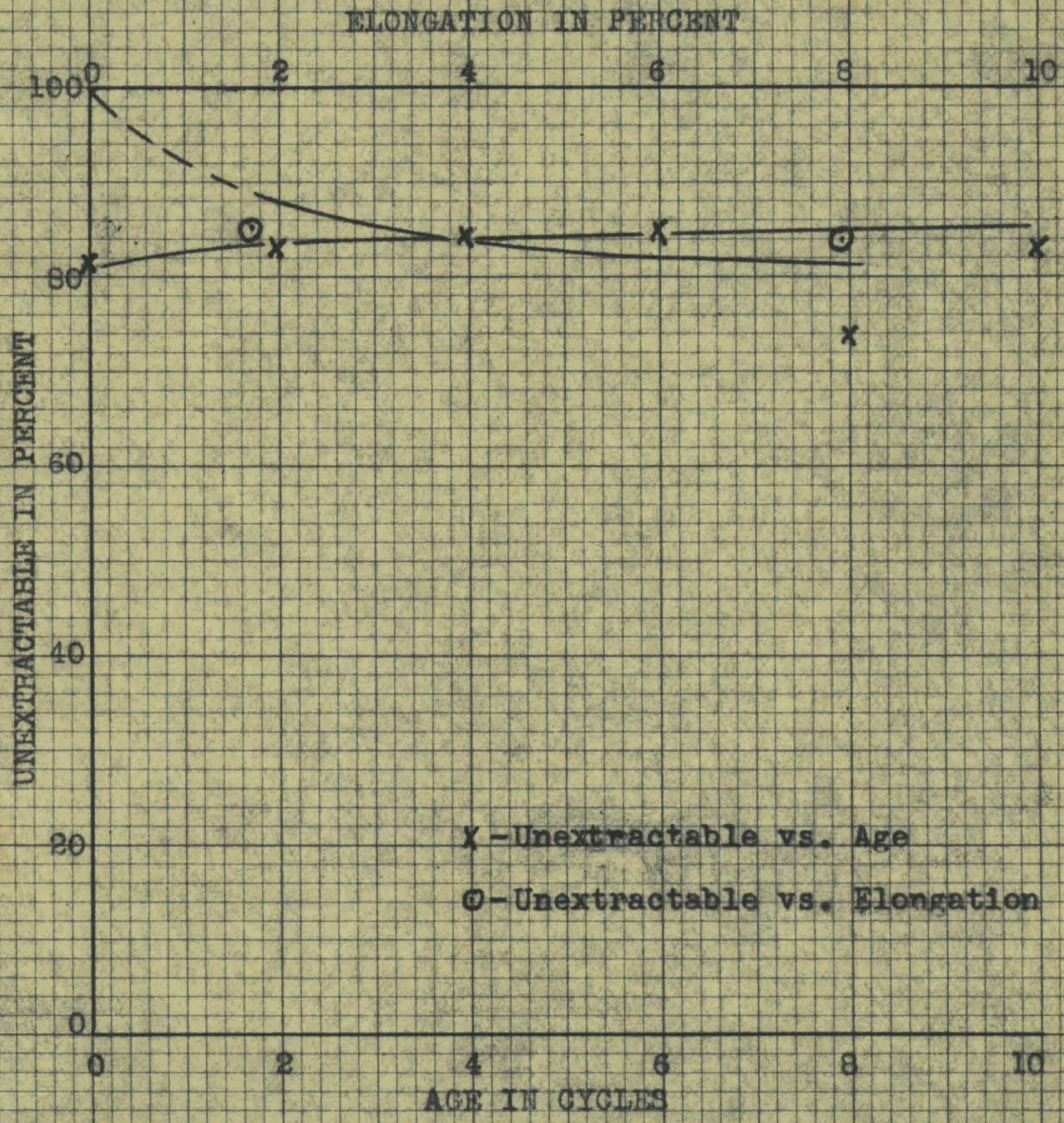

FIG. 30. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 16 GALLON LINSEED OIL-BAKELITE VARNISH.

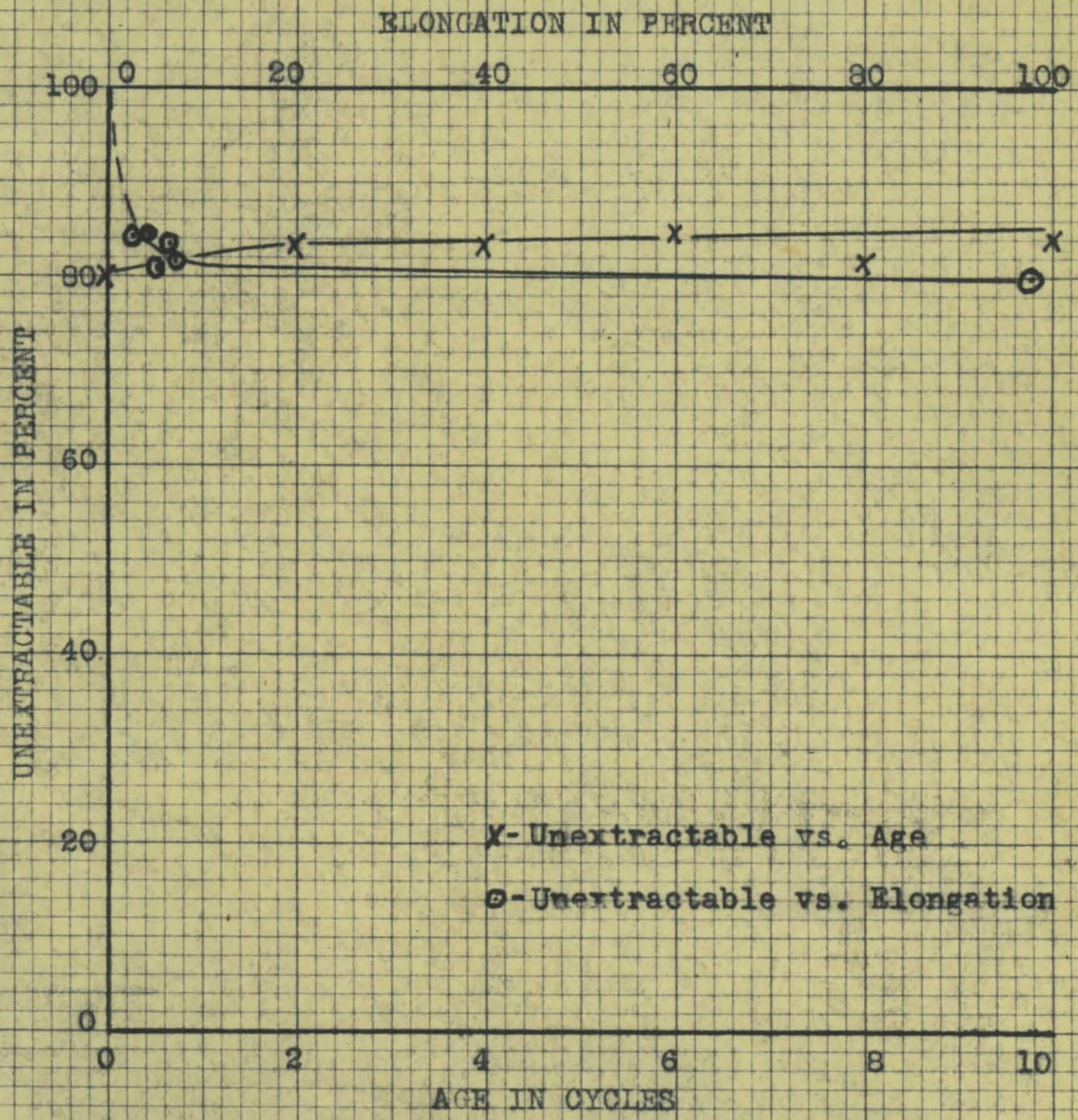

FIG. 31. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON LINSEED OIL-BAKELITE VARNISH.

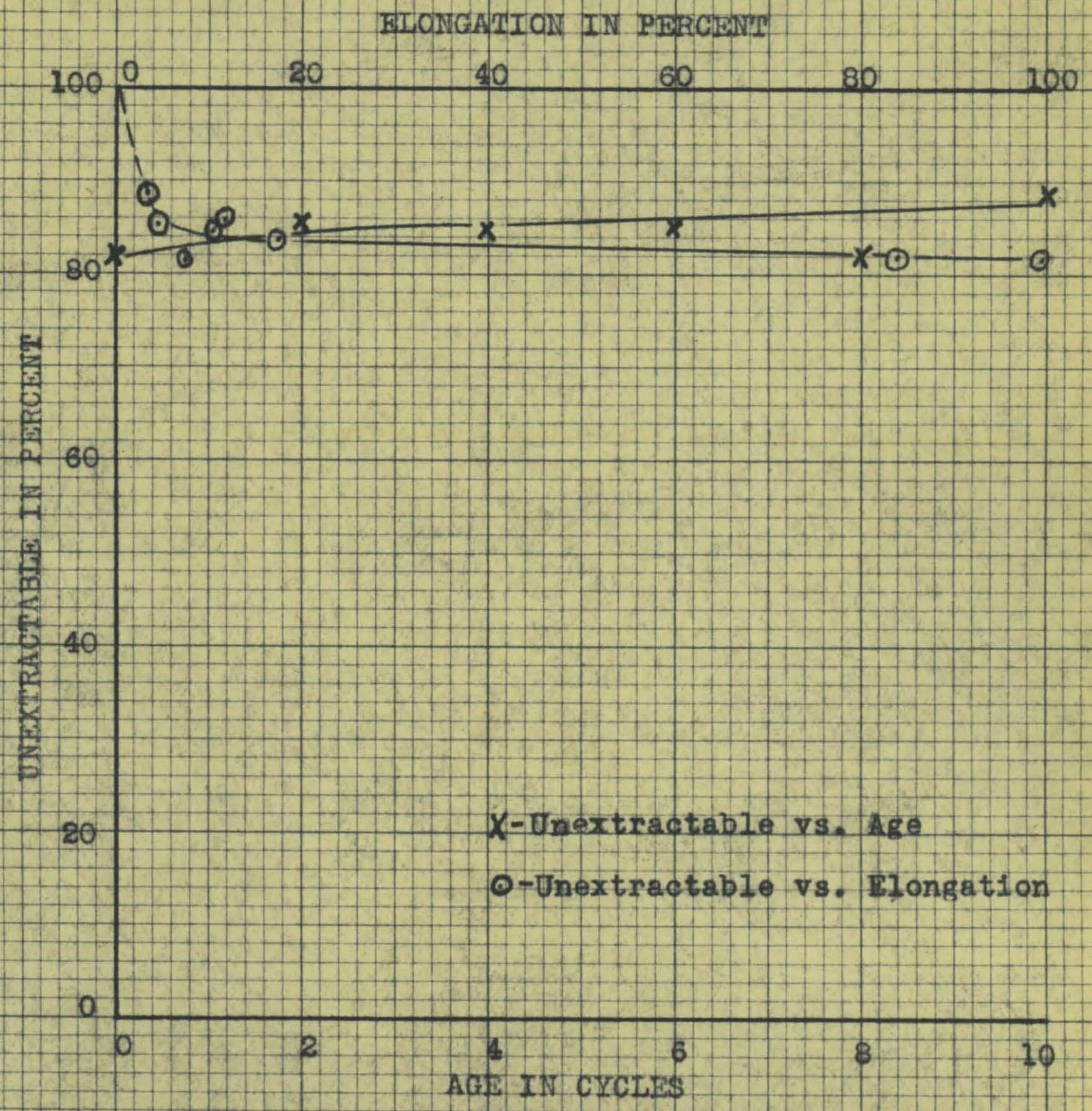

FIG. 32. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON LINSEED OIL-BAKELITE VARNISH.

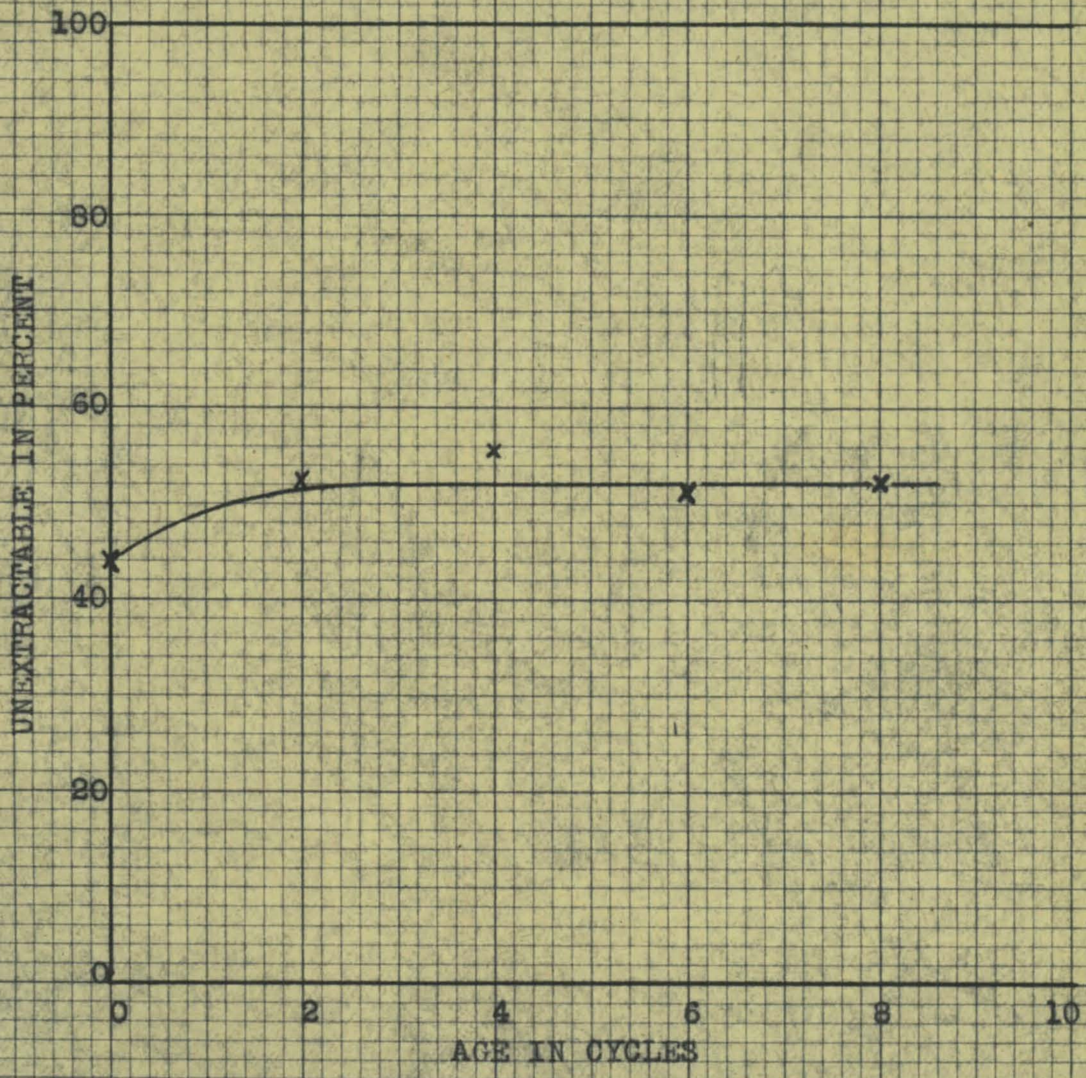

FIG. 33. PERCENT UNEXTRACTABLE vs. AGE FOR 16 GALLON LINSEED OIL-NEVILLITE VARNISH.

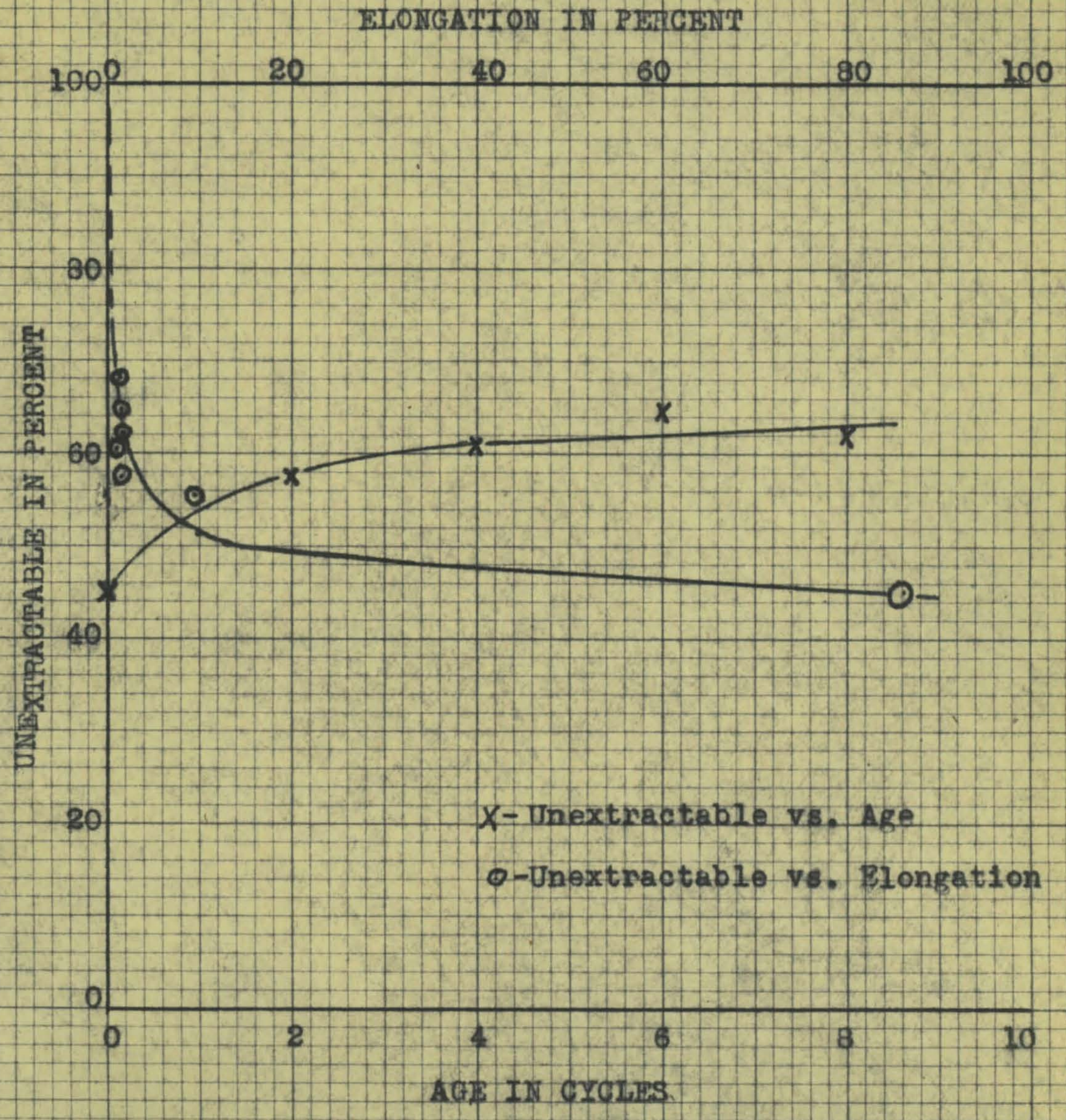

FIG. 34. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON LINSEED OIL-NEVILLITE VARNISH.

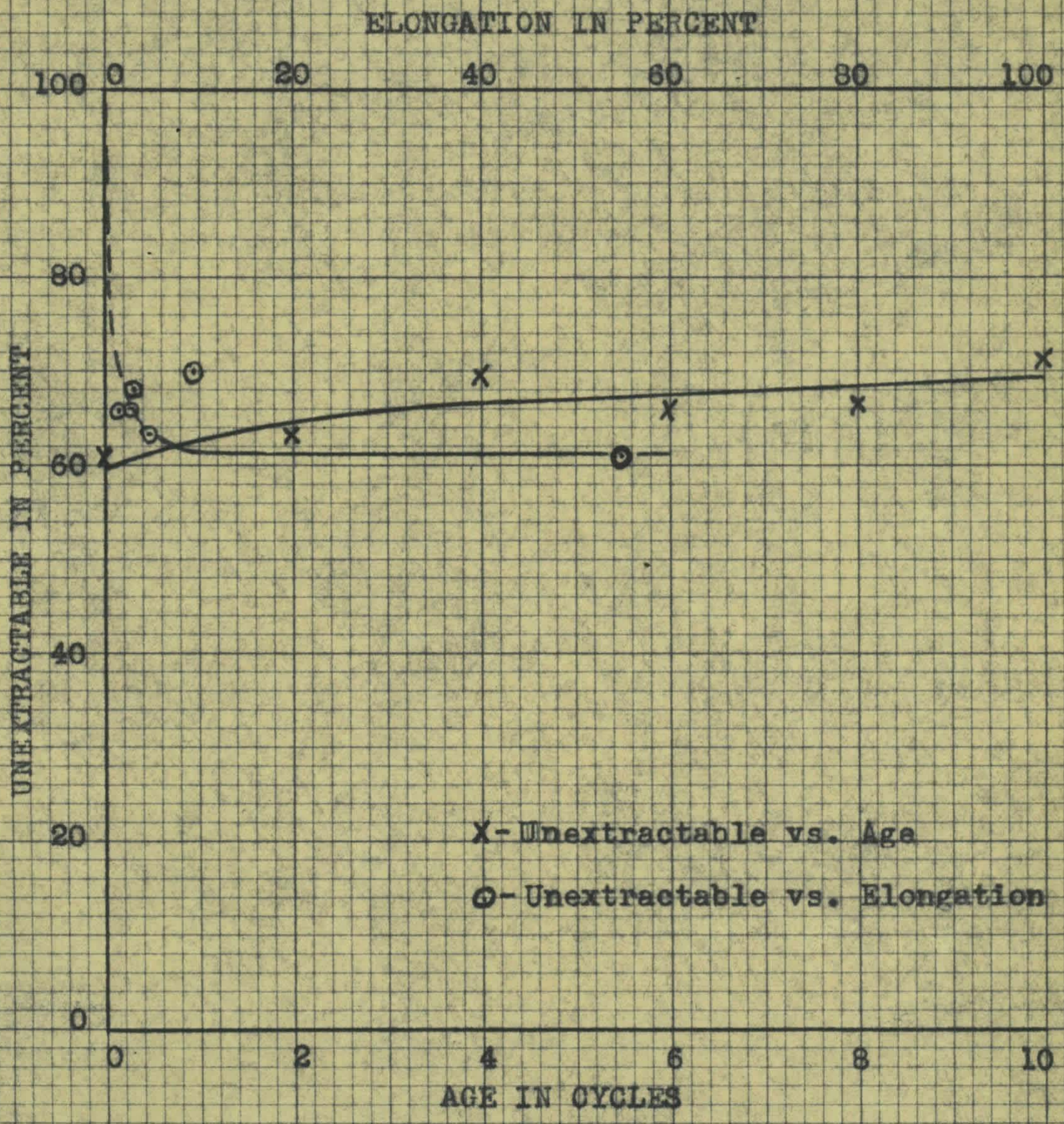

FIG. 35. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON LINSEED OIL-NEVILLITE VARNISH.

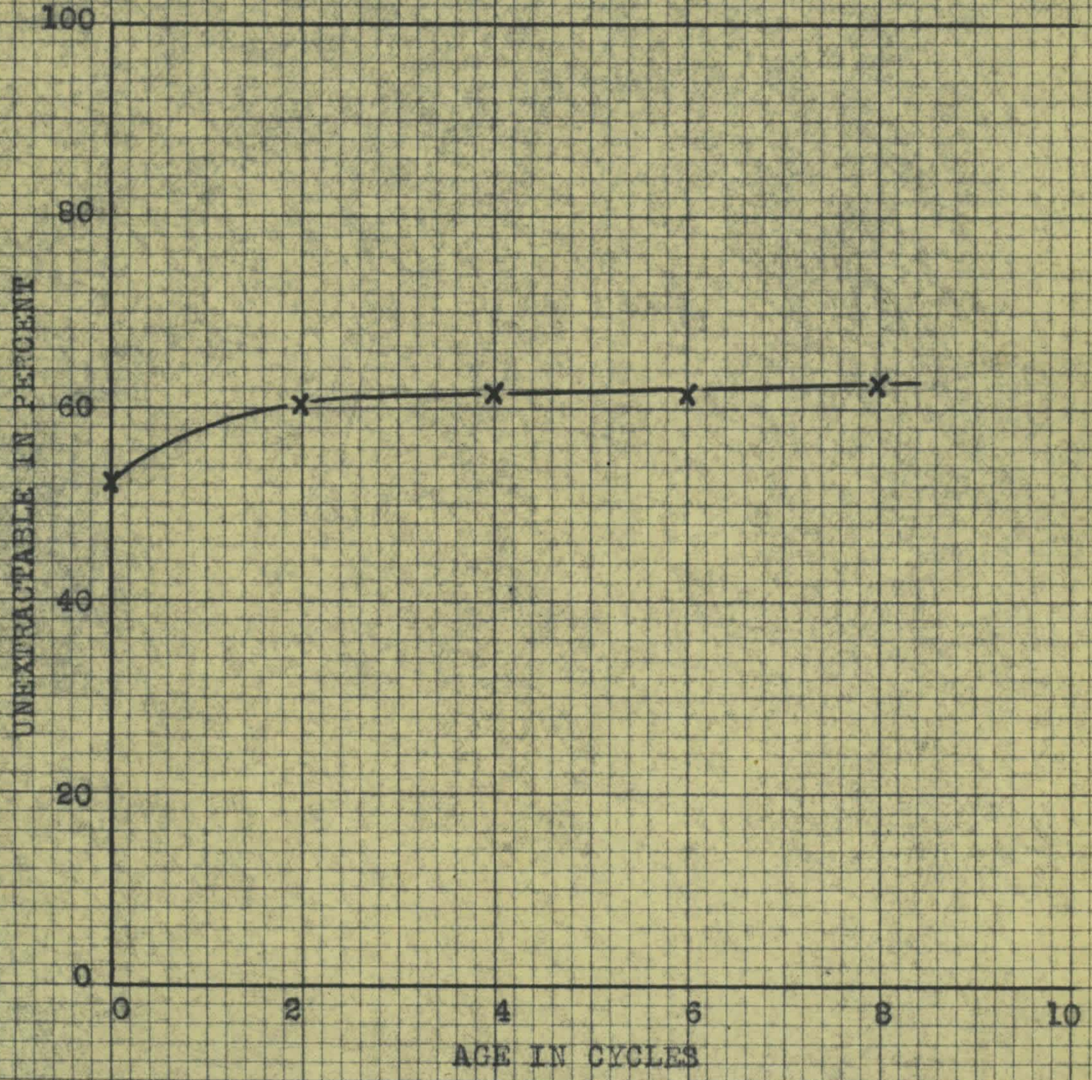

FIG. 36. PERCENT UNEXTRACTABLE vs. AGE FOR 16 GALLON LINSEED OIL*ESTER GUM VARNISH.

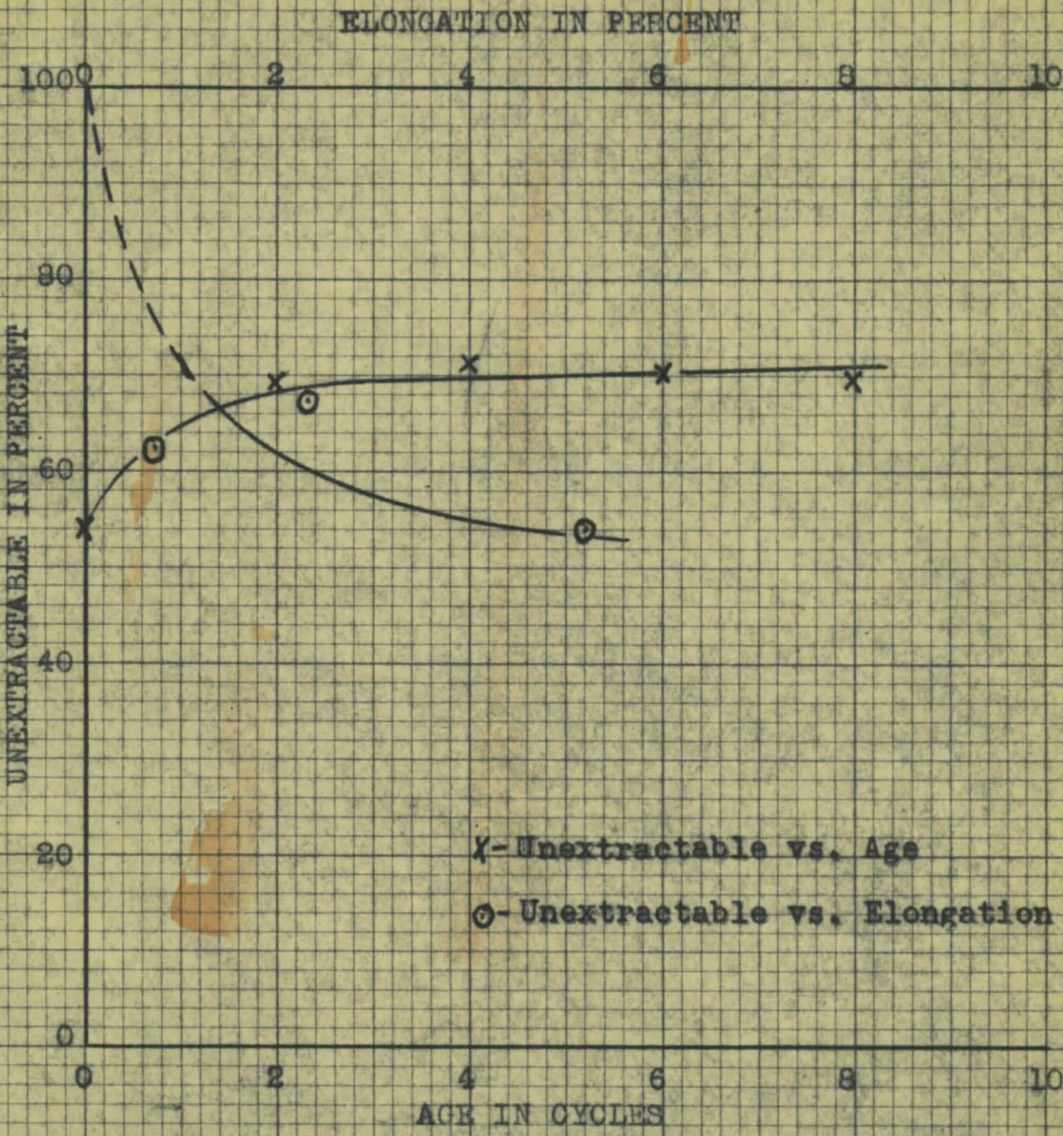

FIG. 37. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 25 GALLON LINSEED OIL-ESTER GUM VARNISH.

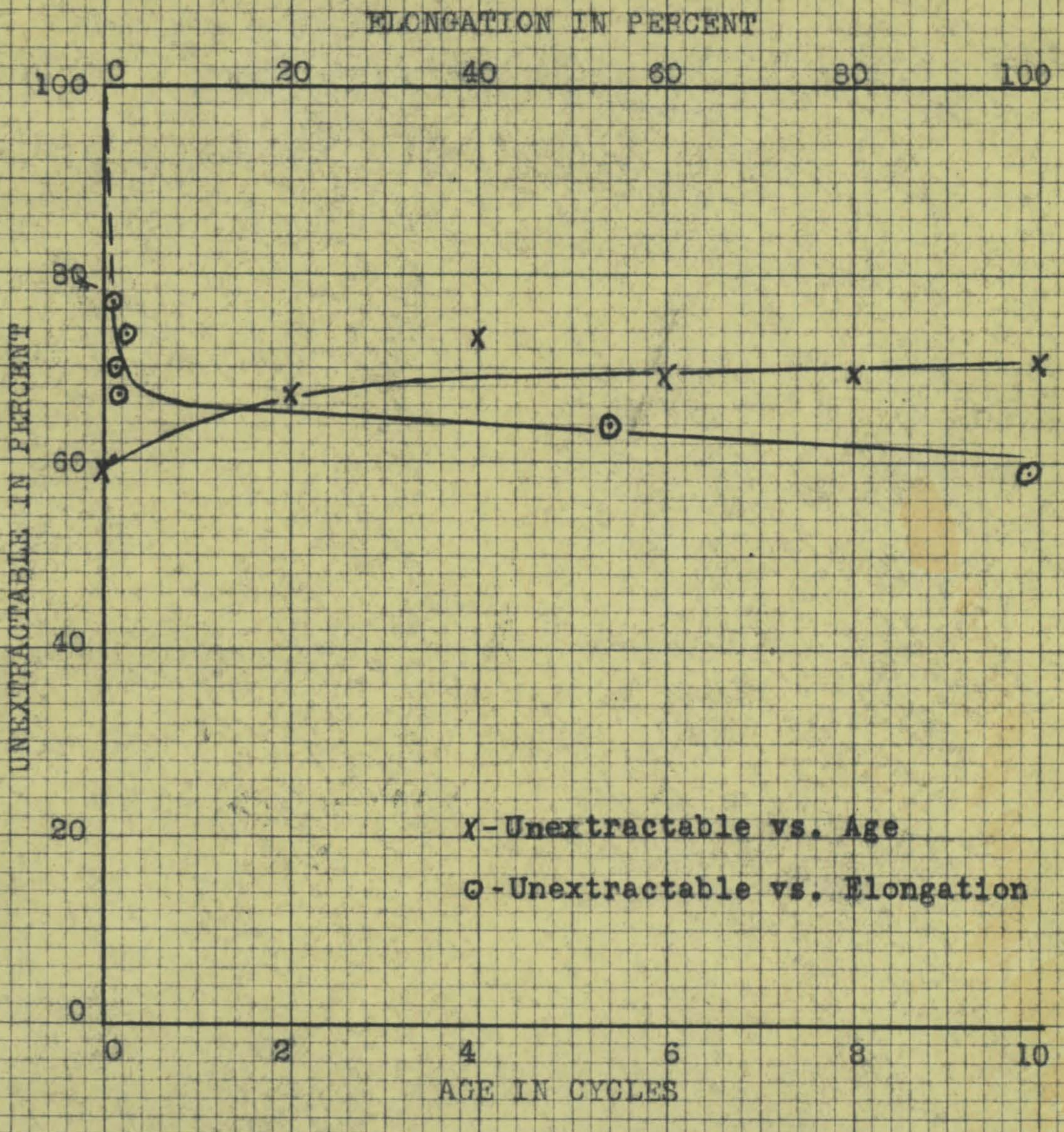

FIG. 38. PERCENT UNEXTRACTABLE vs. AGE AND ELONGATION FOR 33 GALLON LINSEED OIL-ESTER GUM VARNISH.

INTERPRETATION OF DATA

A study of the curves, figure 7-38, shows that the polymer content of the varnish films increases with age until it reaches an almost constant value. The rate of polymerization is more rapid during the early life of the film and approaches zero as aging progresses to the point of failure.

The most noticeable feature indicated by these curves is the effect on the polymer content of changing the resin type. When considering films formulated with the same oil, and of comparable oil length and age, the polymer content is lowest in the case of the Nevillite resin varnishes. Ester gum films are somewhat higher in polymer content, and the oil-reactive resins, Bakelite and glycerol phthalate, produce films which are of much higher and approximately equal polymer content. This phenomenon is in keeping with the known fact that Bakelite and glycerol phthalate resins increase the rate of heat-bodying of oils while ester gum retards bodying. When cooking the Nevillite varnishes, it was noted that this resin exhibited a retarding effect upon the bodying of the oils to an extent equal to or greater than did ester gum.

Varnishes formulated with the same resin but with different oils show a similar variation in the polymer content of their films at corresponding oil lengths and ages. In general, the linseed oil varnishes produced films which were lower in polymer content than chinawood oil films, while similar castor oil films showed the highest polymer content. This variation in polymer content is comparable to the rates of heat-bodying of the oils. Dehydrated castor oil bodies faster than does calorized chinawood oil, while linseed oil bodies at a rate slower than either of the others.

Variation in the oil length of the varnishes produced an effect upon the polymer content similar to change in the resin type. At the point of film failure, the polymer content varied considerably with the oil length in the case of the Nevillite and ester gum varnishes, and to a much lesser extent in the case of the Bakelite and glycerol phthalate varnishes. This is attributable to the reactivity between the resins and the oils. The retarding effect of the Nevillite and ester gum resins was considerable in the shorter oil length varnishes, but was not so noticeable in the longer oil lengths, since the concentration of the resin was greatly diminished. However, since Bakelite and glycerol phthalate enhance the polymerization of drying oils, the shorter oil length films were nearly equal in polymer content to the longer oil length films, and in the case of the Bakelite-castor oil films, the 16 gallon film had a higher polymer content at failure than did the 33 gallon film. This condition might have been due to the high resin concentration, and consequently, the acceleration of polymerization, in the 16 gallon varnish, but since the difference is within the limit of experimental error, it would not be proper to accept this surmise as factual.

The evidence presented by figures 7-38 and Table VII appears to reject the theory that the failure of an oleoresinous film occurs when the polymer content of the film reaches a definite value. The range in polymer content at failure (92 per cent for the 16 gallon castor-oil-Bakelite varnish to 32 per cent for the 16 gallon linseed oil-Nevillite varnish) is too great to conceive of experimental error as the cause. If the theory proposing failure due to the formation of three-dimensional polymer is to be held at all, it apparently must be modified to include provision for the type of polymer occurring.

There is good reason to believe that different types of highly polymerized molecules are formed when a reactive resin is cooked with a drying oil, and when a nonreactive resin is cooked with the same drying oil. According to Bradley (13), the cross-linked or three-dimensional molecule is insoluble in ordinary solvents such as acetone, and the linear, two-dimensional molecule is soluble. In the case of the Nevillite and ester gum varnishes, a large percentage of the soluble, linear film material is present at failure. However, the linear film material, while still soluble, is apparently rigid enough so that film failure occurs when the total of three-dimensional and two-dimensional film material becomes sufficiently great. This assumption must be made in order to retain the idea that failure is caused by the formation of a rigid molecular structure.

A study of the distensibility data for the films formulated from Bakelite lead to the conclusion that this property is not an accurate guide to the durability of an oleoresinous film. The per cent elongation of many of the Bakelite films was so low that it was impossible to strip the free film from the amalgamated tin panel. Other films having high tensile strength would break under the distensibility test without recording any elongation. All these films were very durable and showed no sign of failure after ten cycles in the accelerated weathering unit. However, films formulated from other resinous material showed visual failure at elongations which could be measured, and which were higher than the elongations of the durable Bakelike films.

CONCLUSION

The investigation of the structure of oleoresinous films by studying the distensibility and unextractable properties of these films has led to the following conclusions:

(1) The theory that failure of an oleoresinous film is caused by the formation of a definite amount of three-dimensional polymer in the film does not apply to all types of oleoresinous combinations.

(2) Films produced by varnishes formulated with oil-reactive resins contain a large amount of three-dimensional polymer while still comparatively fresh, although films prepared from varnishes formulated with non-reactive resins or resins which retard polymerization still contain a large amount of two-dimensional film material at failure.

(3) If film failure is caused by the presence of a rigid molecular structure in the film, linear as well as cross-linked molecules contribute to the rigidity of the structure.

(4) Distensibility of an oleoresinous film as measured by mechanical methods is not a proper indication of the durability of the film.

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