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UNIVERSITY OF LOUISVILLE

THE EFFECT OF PIGMENTS ON OLEORESINOUS FILM STRUCTURE
"

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

Glenn Robert Eudaley Jr.
"

1942.

THE EFFECT OF PIGMENTS ON OLEORESINOUS FILM STRUCTURE

Glenn Robert Eudaley Jr.

Approved by the Examining Committee:

Director

May 14, 1942.

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ABSTRACT

The purpose of this investigation is to determine the effect of certain pigments on the structure of varnish films, and to ascertain whether pigment can be substituted for resin in the formulation of oleoresinous coatings.

Enamels were prepared by replacing different volumes of resin in the varnishes with an equal volume of pigment. The resulting enamels were cast into films which were weathered. The aged films were then tested for distensibility and finally extracted with acetone.

It was concluded that for pigment concentrations of fifty percent all pigments could be substituted in the varnishes containing resin of the insoluble type without any change in polymer content at failure. For varnishes containing resin of the soluble type this substitution was only possible for titanium dioxide. The reactive pigments made the failure-polymer increase into the range of the insoluble resin type varnishes.

It was found that for enamels in which the pigment concentration was less than fifty percent the substitution of pigment for resin caused abrupt decreases in the value of the polymer content at failure. This was attributed to the fact that the pigments were not present in concentrations high enough to exhibit their true effect.

INTRODUCTION

The character of oleoresinous films has been under investigation (4,5) in this laboratory for several years. It has been established that an oleoresinous film can be separated into two constituents by acetone extraction. The first of these constituents is made up of highly complex, three-dimensional polymers (polymer) which represents the film forming material. The second of these constituents is made up of non-polymerized or lowly polymerized material (non-polymer) which represents the plasticizer portion of the film. It is the value of this polymer to non-polymer ratio that was studied throughout the life of the film.

The previous investigators (4,5) found that the value of the polymer content of an aging film increased rapidly from its initial value during the early life of the film. They found that the value of this polymer to plasticizer ratio increased less rapidly as the film becomes older, until finally a constant value was approached as the film neared failure.

It was revealed that the percent elongation of a film is large (on the order of 100 percent) after the film was freshly prepared and the polymer content was low, but that it decreases and approaches a minimum value as the polymer content reaches its maximum constant value. In fact, it is this diminishing of the film distensibility (indicated by the percent elongation) that causes the film to fail.

The experimental work up to this time has considered, principally, clear varnishes. It is the purpose of this investigation to extend the work to pigmented varnishes or enamels, in an effort to determine the effect of pigments on the varnishes that were studied previously. It is desired to classify the pigments under consideration according to their polymerization effects, as the previous investigators (4) did for resins. This work is to be done by replacing with pigments certain volumes of resin in varnishes whose behavior on aging is known. These new enamels are to be aged and the values of the polymer content and the percent elongation are to be determined during the life of the film. These new values will then be compared and classified in order to ascertain the role of pigments in oleoresinous film structure.

HISTORICAL

It is well known that the nature of a pigment present in a paint has a distinct influence upon the rate of drying of the paint and upon the characteristics of the film obtained after drying.

Sabin (29) compared the drying curves of raw linseed oil, bodied linseed oil, and pigmented raw linseed oil films. The pigmented oils were mixed in the ratio of one-fourth gallon of pigment to three-fourths gallon of oil. He found that the curves of the pigmented oil and the raw oil films followed the same general trend and the pigmented oil liberated decomposition products during the entire period of drying. He further observed that the change in weight undergone by a paint film during drying depended on the nature of the pigment present in the paint.

Gardner (6) postulated the evolution of organic acids of a fatty or aromatic nature, carbon dioxide, aldehydic substances, and slight amounts of carbon monoxide from drying paint films. It was observed that basic pigmented films were more active in this respect.

King (9) investigated the evolution of volatile products from clear and pigmented linseed oil films and concluded that the clear oil films evolved as much material as the oil and pigment mixture.

Rhodes and Van Wirt (27) investigated the effect of various pigments upon the rate of oxidation of linseed oil. Films were prepared by coating strips of cloth two centimeters wide and ten centimeters long with a linseed oil paint that contained 0.2 percent lead drier

and various pigment-oil-mixtures of 40 percent pigmentation. The painted strips were weighed and hung inside an Erlenmeyer flask, the air was displaced with oxygen, and the flask was connected to a manometer in such a manner that the difference in levels gave a measure of the oxygen absorbed. By removing the cloth strips and reweighing them, it was possible to calculate the apparent loss in weight due to volatile products.

They (27) concluded that the drying of linseed oil was an autocatalytic reaction, the catalyst being an oxidation product of the oil itself. They further concluded that the well-known effect of lead salts in accelerating the drying of oil is due to the fact that these salts act as pseudo-catalysts to promote the formation of autocatalysts and thus increase the oxidation rate.

Rhodes and Van Wirt divided pigments into three groups. The first of these, of which silox is an example, had little or no effect on the oxidation of the films investigated. The second group, which included such apparently dissimilar substances as leaded zinc, lithopone, titanox, and barium sulfate, slowed down oxidation and materially affected the amount of oxygen absorbed and the amount of volatile matter given off. The third group of pigments included those which tend to increase the amount of oxygen absorbed by the oil and the amount of volatile matter given off. This group includes such pigments as basic lead carbonate and basic lead sulfate.

The oxidation curves of bodied and raw Chinawood oil were investigated (25). The investigators concluded that the drying of tung oil, like the drying of linseed oil, was an autocatalytic reaction, accelerated by soaps of lead, manganese, or cobalt.

Rhodes and his co-workers (22, 23, 24, 26) found that lampblack and carbon black markedly inhibited the oxidation of raw linseed, because of the adsorption on the pigment of an intermediate oxidation product, which is the true catalyst in the drying of linseed oil. They found that red iron oxide pigments tend to accelerate the oxidation of linseed oil in paint films, partially hydrated iron oxide being more active than the anhydrous, while the presence of calcium carbonate rendered both forms less active. Black iron oxide was found to be relatively inert, retarding slightly the oxidation of the oil. Zinc oxide (pure) had no effect on the oxidation rate and the presence of soluble compounds of zinc caused the linseed oil to coagulate at an earlier stage in the oxidation to form a harder less permeable film. Ochres tended first to retard and then to accelerate the drying of the oil. Initial retardation was caused by absorption of the drier from the oil; the final acceleration was due to the formation of iron soaps which act as catalysts. However, this reaction is less active than that of red iron oxide. Siennas and umbers show less effect on the initial rate of oxidation of the oil than did ochre, because the removal of the lead drier is compensated by the formation of a small amount of Manganese drier.

Extensive work on the structure of oleoresinous films has been carried on in these laboratories for the last three years, this paper being the third in this series. The initial investigation was carried on by Ernst and McQuilkin (5). They worked with varnish films prepared by cooking Congo resin with bodied linseed oil and calorized tung oil in 8, 16, 25, and 33 gallon lengths and enamel films prepared by grinding titanium dioxide in the above varnishes. The changes taking place in the 'polymer' to plasticizer ratio were studied during the life of the film as well as the distensibility changes. It was observed that failure, as indicated by minimum distensibility, occurred when the concentration of the polymer, as indicated with extraction with acetone, reached a value lying between 70-80 percent. 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 re-active.

This fundamental research was extended by Ernst and Lubbers (4), so that it included varnishes formulated from typical drying oils and several synthetic resins chosen particularly because

of their variation in oil reactivity and chemical type. The oils were bodied linseed oil, calorized tung oil, and dehydrated castor oil. The resins chosen were ester gum, a phenol-formaldehyde resin (Bakelite #254), a cyclo-paraffin-napthene polymer (Nevillite #2), and an oil-modified glycerol phthalate resin. Each oil was cooked with each resin in 16, 25 and 33 gallon lengths. Films cast from the resulting varnishes were weathered for successive periods, elongated, and extracted with acetone. The polymer content was correlated with the age of the film and the percent elongation, and it was found that the varnishes could be divided into two classes according to the resin contained.

The first class contained resins of the 'insoluble' type, namely, Bakelite #254 and the oil-modified glycerol phthalate resin. These resins are insoluble in acetone per se, and tend to promote polymerization to the extent that the value of the polymer content at failure of varnishes formulated with these resins lies very close to 88 percent. The other class was composed of resins of the 'soluble' type, namely, Nevillite #2 and ester gum. These resins are acetone soluble and tend to retard polymerization so that the value of the polymer content at failure of varnishes formulated with them varies over a relatively large range according to the oil length and the individual materials used. These values were found to average around 75 percent.

The oils investigated were also ranked in the following order according to their tendency to promote polymerization: castor, first; tung, second; linseed, third.

Various other investigators previous to those already mentioned have studied the mechanism of the formation and deterioration of oleoresinous films. Overholt and Elm (19) 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 (20,21) with glycol and glycerol esters of 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 (13) investigated the aging of pure trilinoleic and trilinolinic 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 the plasticizer from polymer in a dried film may be accomplished by solvent extraction. The best solvent was acetone. Bradley and Pfann (1)

studied the heat-bodying of oils and concluded that both intermolecular and intramolecular reactions proceeded, and partial thermal decomposition of the esters also occurred. 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 percent of the weight of the gel.

Rose and Bolley (28) divided linseed oil 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 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.

THEORETICAL

Although the problem regarding the mechanism of film formation is of long standing and has received extensive treatment in the literature, it may be summarized by stating that the resinous state must be developed before a film can be formed. The primary characteristic of the resinous state is the presence of very large molecules. These large molecules may be configurations of long chains, closed chains, or chains of cross-linked character.

The conceptions regarding the resinous state have become much clearer because of intensive research (3,8,2,30) carried on in the field of synthetic resins during the past decade. Along with large molecules come the phenomena of molecular complexity and large molecular surface area. No matter whether the molecule be a long chain, a closed chain or a cross-linked structure, the opportunity for self-addition of repetitive units and/or polycondensation becomes tremendous as the molecule grows larger. As this happens, steric hindrance, wall effects, and local poisons interfere with further growth, and consequently the size of the molecules in a given mass of resin varies over a wide range.

The effect of large molecular surface area is to present an unusual opportunity for molecular surface forces to come into play. Van der Waals forces at these surfaces can produce solvation, association, and aggregation effects, by means of which

molecules may associate into micellar structures or may adsorb foreign molecules with great tenacity.

According to Keimle (8) each reacting molecule must have at least two reactive points in order to form a resin. If they have a 2:2 functionality, the polymer will have a chain configuration and will be a permanently soluble and fusible thermoplastic resin. However, if the molecules have a functionality greater than two, cross-linking will occur and a non-fusible, insoluble, thermalsetting polymer is formed. This three-dimensional interlinking reduces to a large extent the high elasticity that characterizes the chain type structure.

The mechanism of the 'drying' reaction of a drying oil is generally considered to be a combination of oxygen absorption and molecular association or polymerization. Although the formation of a solid film is dependent on absorption of oxygen, the wet film on exposure to air does not immediately take up oxygen. The length of this initial induction period (31) is governed by traces of antioxidants in the oil and is appreciably shortened by the addition of metallic driers. The oxygen absorption is considered by most investigators (14, 10, 18) to form peroxide linkages at the double bonds. During the early oxidation period, volatile oxidation products are split off, among which short-chain aldehydes, acids, oxides of carbon, and water have been identified. Increased drier content furthers the formation of these volatile products. This

initial oxidation primarily serves to increase the polarity of the drying oil molecules, which favors the formation of interlinkages with other molecules.

There are many controversial data and opinions concerning the exact nature of this interlinking process. There are two types of polymerization reactions which might take place. The first is the combination of unsaturated compounds by primary chemical linkages to form larger molecules, true polymerisation. Marousson (15) explains this phenomenon on the basis that true polymerides are formed across oxygen bridges. It is also postulated (15) that the polymerisation takes place through the primary valence forces of the peroxide groups.

The second type of polymerization possible is the combination of unsaturated compounds through secondary or residual valencies. This is called colloidal association and is the reaction toward which the latest experimental work points (14, 18). The associating or polymerizing reaction brings about gelation of the oil and immobile film formation. At this point no further chemical reaction by way of oxygen absorption can be detected. A gel has been formed, which consists of a continuous solid phase surrounded by a liquid phase of essentially identical chemical composition. Further aging brings about the gradual increase of the solid phase at the expense of the absorbed but

extractable liquid phase. As the three-dimensional linking becomes more complete, the film increasingly loses high distensibility and ultimately becomes brittle.

The broadest classification of the components making up an enamel would be vehicle and pigment. The vehicle constitutes the continuous phase and the pigment the disperse or discontinuous phase. The vehicle must be a resin and oil mixture or a straight synthetic resin solution. This paper is limited to vehicles in the former category.

It is well known that pigments have certain physical effects on clear varnish films. Pigments impart coloration, opaqueness, and the ability to exclude ultra-violet light. The coating may also be strengthened, hardened, and made more impervious to moisture permeation. These effects produce increased durability.

A prime requisite of all pigments is that the size of the individual particle be small. This is necessary in order to provide a large surface area, increase wetability, and bring about ease and stability of dispersion. The majority of pigments fall within a range of 0.1 to 5.0 microns in average diameter. However, this is a large figure in comparison with the size of the molecules in which the pigment must be dispersed. For example an oleic triglyceride molecule has a length of 0.00123 microns (12) and an

area of 127×10^{-8} microns squared. Thus the comparison shows that the size of a pigment particle is on the order of one-thousand times the molecular size of its initial dispersing medium. The size of the polymer molecule in which the pigment is ultimately dispersed is undetermined but is known to have become tremendous.

Since the size of the pigment particle is comparatively large it follows that the particles will be securely bound in the network of three-dimensional, cross-linked polymer that is formed when an enamel film ages. For this reason the pigment may be counted as polymer in the following experimental consideration, since there exists little chance of its being 'washed' out of the polymer network by the extracting solvent, acetone. This is true for pigment in the unreacted form. It is possible for some of the pigments to react with the oil in the varnish to form metallic soaps, such as lead soaps or iron soaps, which may be easily extracted.

The pigments may have other effects on the films besides adding to the bulk of insoluble material. The pigments under consideration in this investigation are inorganic salts and oxides of lead, iron, titanium, and cadmium. It is known (22, 27) that the lead salts, and iron, to a lesser degree, bring about acceleration of the oxidation of a film and increase the total amount of oxygen absorbed. It was shown by these same investigators that titanium

dioxide had exactly the opposite effect, retarding the oxidation and decreasing the total amount of oxygen absorbed.

Since oil polymerization of oleoresinous films is a function of oxidation the polymer content or percent unextractable of a film may be expected to be a function of the oxidation. In other words, the final value of the polymer content or the polymer content at failure should be a function of the total amount of oxygen absorbed by the film on aging.

Therefore the films pigmented with lead and iron pigments should show values of polymer content at failure, higher than those obtained for unpigmented films and films pigmented with titanium dioxide. Also films pigmented with titanium dioxide should polymerize less than those containing no pigment. The effect of the cadmium pigment can not be postulated at this time, not only because of the scarcity of experimental data on the nature of cadmium pigments (re, film structure), but also because the particular cadmium pigment used in this investigation is one that tends to flocculate instead of disperse in ordinary vehicles.

The effect of pigments on film distensibility, considered from a film structure angle, tends to complicate the structure of the film. An increase in the complexity of the film network might tend to decrease the elasticity of a film, just as an increase in the amount of three-dimensional, cross-linked polymer does.

If the problem is approached from a practical point of view the answer appears to be different. It is generally accepted that pigmented films are more durable than unpigmented films. However, Konig (28) and others contend that the life of a film depends on its ability to undergo strains and stresses set up by contractions and expansions occurring within the film and within its supporting material because of temperature changes or other causes. This ability should be dependent on the distensibility of the film. Thus the more durable enamel films should have greater distensibility.

EXPERIMENTAL

RAW MATERIALS.

The raw materials selected for this investigation included several typical inorganic pigments chosen because of their variation in chemical and physical nature, some typical varnishes taken from the previous investigation (4), drying oils to blend with the pigment-varnish mixtures in order to obtain the correct oil length, and thinners suitable for thinning the formulations to the desired consistency.

The pigments used were pure titanium dioxide, having a specific gravity of 3.88, a bulking value of .03118, and an oil absorption of 24.2; basic carbonate of white lead, having a specific gravity of 8.7, a bulking value of .0179, and an oil absorption of 9; lead chromate (chrome yellow), having a specific gravity of 6.01, a bulking value of .01998, and an oil absorption of 17.7; precipitated red iron oxide (99% Fe_2O_3), having a specific gravity of 5.15, a bulking value of .0240, and an oil absorption of 32.5; and a commercial cadmium yellow, having a specific gravity of 4.55, a bulking value of .02759, and an oil absorption of 23.5.

The basis on which the varnishes were chosen was to pigment and analyze as few samples as possible, yet still realize all the different effects that were possible from the varnishes studied last year (4), viz. short oil varnish containing soluble

resin, short oil varnish containing insoluble resin, long oil varnish containing soluble resin, short oil varnish containing insoluble resin, plus variation of drying oil. The varnishes used in this investigation included 16 gallon linseed oil-Bakelite #254, 16 gallon tung oil-Bakelite #254, 16 gallon linseed oil-ester gum, 33 gallon linseed oil-Bakelite #254, 33 gallon linseed oil-ester gum, and 16 gallon dehydrated castor oil-Bakelite #254.

The drying oils used are those inherent in the varnishes just mentioned, namely, 2-3 bodied linseed oil, A.D.M. No. 50 calorized chinawood oil, and dehydrated castor oil (Synthenol). The thinners used were mineral spirits, having a specific gravity of 0.791 and a boiling range of 153-204°C., and xylene, having a specific gravity of 0.865 and a boiling range of 138-144°C. Mineral spirits was used to thin the enamels containing ester gum, while xylene was used to thin the enamels containing Bakelite #254 resin.

Drier was also added to the formulations in the form of regular Nuodex lead, manganese, and cobalt driers, containing 24, 6, and 6 percent metal, respectively. They were added to the enamel formulations on a metal to oil-added weight basis of 0.30 percent lead, 0.03 percent manganese, and 0.015 percent cobalt.

The mechanism of enamel formulation was effectively to replace one-half, three-tenths, and seven-tenths of the varnish

resin volume with pigment volume. That is to say from each varnish-pigment combination three enamels were made, one having a pigment-resin volume ratio of 5/6, one having the ratio of 3/7, and one having the ratio of 1/9. For the purpose of clarification the formulation of one of the enamels be considered TLB1-5. This code formula refers to a 16 gallon, linseed oil-Bakelite #254 varnish, pigmented with titanium dioxide so that the pigment-resin volume ratio of the ultimate enamel is 5/6.

The analysis of the varnish is

Linseed oil	-	28.55 %	(wt.)
Bakelite	-	22.25 %	(wt.)
Xylol	-	49.20 %	(wt.)

The composition desired in the finished enamel on a volume basis is

Linseed oil	-	16 volumes
Bakelite	-	5 volumes
TiO ₂	-	5 volumes

This composition is transferred to a weight basis by multiplying the volume of each constituent by its specific gravity

Linseed oil	-	16(.99)	=	15.84 weight units
Bakelite	-	5(1.2)	=	6.00 weight units
TiO ₂	-	5(3.9)	=	19.50 weight units

Since it is obviously impossible to take resin out of the varnish, it is necessary to add oil and pigment to the varnish to get the desired combination. All the resin in the finished enamel must come from the varnish; therefore a quantity of varnish corresponding to 6.00 weight units of resin must be taken as a starting material

amount of varnish = $6.00 / .2225 = 26.96$ weight units

But this amount of varnish will also furnish a quantity of oil

$$\text{quantity of oil} = 26.95(.2855) = 7.68 \text{ weight units}$$

The amount of oil desired is 15.84 weight units; therefore some oil must be added to make up this difference

$$\text{amount of additional oil} = 15.84 - 7.68 = 8.16 \text{ weight units}$$

The amount of pigment added is the same as previously calculated.

Therefore the actual composition of the formulation is

16 gallon linseed-Bakelite varnish	- 26.95 weight units
linseed oil	- 7.86 weight units
TiO ₂	- 19.50 weight units

This is the way the formulations were calculated with the exception of thinner and drier. The amount of thinner necessary is calculated in a similar manner and is equal to a quantity necessary to give the final enamel the same volume percent of solids that the original varnish had. The determination of the drier added is made by a simple weight ratio.

The formulations considered in this investigation are shown in Table I. Let it be emphasized that each horizontal entry in the table represents three enamels, having pigment-resin volume ratios of 5/5, 3/7, and 1/9 respectively.

The formulations listed in Table I were not chosen in a haphazard manner, instead, they were selected with the idea of covering the problem adequately, without running more samples than could be handled. The formulations bring about the following changes in enamel makeup: change of resin, soluble to insoluble, change of pigment, reactive to non reactive, change of oil-length, and change of drying oil.

TABLE I
FORMULATIONS

Code No.*	Oil	Oil Length	Resin	Pigment	Thinner
TLEl-5,3,1	Linseed	16	Bakelite	Titanium dioxide	Xylene
BLEl-5,3,1	Linseed	16	Bakelite	BCWL	Xylene
YLEl-5,3,1	Linseed	16	Bakelite	Lead chromate	Xylene
RLEl-5,3,1	Linseed	16	Bakelite	Iron red	Xylene
TTBl-5,3,1	Tung	16	Bakelite	Titanium dioxide	Xylene
BTBl-5,3,1	Tung	16	Bakelite	BCWL	Xylene
YTBl-5,3,1	Tung	16	Bakelite	Lead chromate	Xylene
RTBl-5,3,1	Tung	16	Bakelite	Iron red	Xylene
TLEl-5,3,1	Linseed	16	Ester gum	Titanium dioxide	Mineral Spt.
BLEl-5,3,1	Linseed	16	Ester gum	BCWL	Mineral Spt.
YLEl-5,3,1	Linseed	16	Ester gum	Lead chromate	Mineral Spt.
RLEl-5,3,1	Linseed	16	Ester gum	Iron red	Mineral Spt.
TLE5-5,3,1	Linseed	33	Bakelite	Titanium dioxide	Xylene

TABLE I (continued)

FORMULATIONS

Code No.*	Oil	Oil Length	Resin	Pigment	Thinner
BLE3-6,3,1	Linseed	33	Bakelite	BCWL	Xylene
TLE3-5,3,1	Linseed	33	Ester gum	Titanium dioxide	Mineral Spt.
BLE3-6,3,1	Linseed	33	Ester gum	BCWL	Mineral Spt.
TLE1-6,3,1	Castor	16	Bakelite	Titanium dioxide	Xylene
BLE1-5,3,1	Castor	16	Bakelite	BCWL	Xylene
CLE1-6,3,1	Linseed	16	Bakelite	Cadmium yellow	Xylene

* First letter designates pigment used, T - TiO_2 ; B - BCWL; Y - Chrome yellow;
R - Iron red; and C - Cd Sulphide

Second letter designates oil used, L - linseed; T - tung; D - dehydrated castor

Third letter designates resin used, B - Bakelite #254; E - ester gum

Fourth number designates oil length, 1 - 16 gallons; 3 - 33 gallons

Fifth number designates pigment-resin volume ratio, 5 - 5/5; 3 - 3/7; 1 - 1/9.

APPARATUS.

The apparatus used in this investigation consisted chiefly of an accelerated weathering unit, a distensibility tester, and a battery of extraction units. Other equipment included a paint mill, a film caster, a dial gauge micrometer, and a constant-temperature, constant-humidity cabinet. All this equipment is described in the following paragraphs.

ROLLER MILL. A three-roll, differential-speed paint-mill was used to disperse the pigments in oil. The cylindrical rolls, 6 inches long and $2\frac{1}{2}$ inches in diameter, were made of stainless steel. The distance between the rolls was adjustable by means of hand screws.

FILM CASTERS. The films for this investigation were cast by means of a doctor blade having a clearance of 0.008 inches. The caster has an overall width of $4\frac{1}{2}$ inches and deposits films $3\frac{1}{2}$ inches wide. These films dried to a thickness ranging from 0.002 to 0.003 inches, depending on the solid content and viscosity of the enamel. The film caster in use is shown in figure 1.

PANELS. All films were cast on 31 gauge coke tin panels 6 X 10 inches in size, having $\frac{1}{4}$ inch holes centered $\frac{1}{2}$ inch from the tops.

ACCELERATED WEATHERING UNIT. Rapid weathering of the enamel films was brought about by the use of an Accelerated-Weathering Unit, Model X-1, manufactured by the National Carbon Company. The unit is in the form of a cylindrical, copper-coated, vertical steel shell,

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

containing a rotating panel rack. This rack has a carrying capacity of sixty-four $3\frac{1}{2} \times 10$ inch panels, and rotates 360 degrees every two hours. Ultra-violet radiation is produced by two carbon arcs which operate alternately. The weathering effect of rain is simulated in the unit by a fine water spray directed against the panels. The unit is shown in figure 2.

REFRIGERATING CABINET. A refrigerating cabinet was operated in conjunction with the accelerated weathering unit to produce the weathering effect of low temperature on the enamel films. The cabinet dimensions are $18 \times 10 \times 10\frac{1}{2}$ inches, and it is cooled by the expansion of ammonia in coils.

CONSTANT-TEMPERATURE, CONSTANT-HUMIDITY CABINET. An insulated box maintained at 70°F . and 50 percent relative humidity served as a constant-temperature, constant-humidity cabinet. The temperature was maintained by a thermostatically operated incandescent lamp heater. Humidity was controlled by the use of a saturated solution of magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in an open pan as suggested by Gardner (7). Such a solution, when contained in an air-tight compartment and held at 70°F ., will hold the atmosphere of the enclosure at 54% relative humidity.

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

Fig. 2. Accelerated weathering unit.

MICROMETER. The thickness of the free enamel films was measured with a Randall & Stickney dial gauge micrometer. The micrometer is graduated in thousandths of an inch and readings can be interpolated to ten-thousandths of an inch. See figure 3.

DISTENSIBILITY TESTER. A Scott Tensile Tester, Model x-5, was used to determine the percent 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 pull of two inches per minute. The upper clamp, balanced by weights, actuated a load recording pointer and dial. The tester has a double operating capacity of 0 to 2 pounds and 0 to 10 pounds. See figure 4.

EXTRACTION UNITS. The enamel films were extracted in Soxhlet extraction units. Each unit 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. The units were contained in five batteries of twelve units each. The batteries were constructed in the form of rectangular wooden boxes lined with asbestos paper, and fitted with removable lids in which holes were cut to receive the extraction flasks. Cylindrical metal reflectors were placed around the flasks to direct the heat from the 75 watt incandescent lamp

Fig. 3. Micrometer.

Fig. 4. Distensibility tester.

heaters. Cooling water for the condensers was supplied through an iron pipe manifold running the length of the unit. See figure 5.

Fig. 5. Extraction batteries.

PROCEDURE.

The general procedure consisted of preparing the enamels, casting the films on panels, and aging them. The panels were then amalgamated and the films stripped free. The free films were then conditioned, elongated, and extracted. Each step is explained below.

PREPARATION OF SAMPLES. As mentioned before, the enamels were formulated from varnish, pigment, oil (the same from which the varnish was prepared), thinner, and drier. The correct portions of oil and pigment were mixed to form a paste. This paste was then passed through the three-roll mill to wet and disperse the pigment particles thoroughly. The paste was passed through the mill three times. The varnish, thinner, and driers were then added and the mixture was agitated thoroughly to obtain a homogeneous mixture.

CASTING OF FILMS. Plate glass panels were leveled, and a few drops of water were spread on the top surface. Tin panels, thoroughly cleaned on the top surface with xylene were firmly pressed onto the wetted glass plates to make the two adhere. This presented a flat, stationary metal surface. The films were then cast with the doctor blade, and a constant, forward pull of 1-2 inches per second was exercised by the operator. All films were cast in duplicate.

WEATHERING. The films were allowed to dry in air for three days after casting or until they were no longer tacky. The panels were then trimmed to $3\frac{1}{2}$ x 10 inches and placed in the accelerated weathering unit. Here they were exposed to the action of ultra-violet light, water spray, and refrigeration for periods of 2, 4, 6, 8, or 10 cycles. The 24 hour cycle used was based on that developed by the Commonwealth Edison Company of Chicago. This cycle is given below:

Weathering Conditions	Cabinet Temperature	Time
Heat, light and water spray	104°F.	4 hours
Heat and light	149°F.	$4\frac{1}{2}$ hours
Heat, light, and water spray	104°F.	4 hours
Water spray	68°F.	2 hours
Rest period	Room	6 hours
Refrigeration period	-4°F.	1 hour
Examination of panels	Room	$2\frac{1}{2}$ hours

As inferred in the table above, the panels were carefully inspected at the end of each cycle for chalking, loss of gloss, checking, cracking, and other forms of failure.

AMALGAMATION AND STRIPPING. After removal from the accelerated weathering unit, the panels were inclined at an angle of approximately fifteen degrees with the horizontal and a drop of mercury was placed on the unprotected metal surface above the top edge of the film. Remaining in this position overnight, the tin surface under the film became amalgamated with mercury. This presented a

surface to which the film did not adhere. On the following day the edges of the film were trimmed with a razor blade and the film was stripped free from the panel.

CONDITIONING. The free films were hung in a constant-temperature, constant-humidity cabinet for three days or more. This caused them to reach temperature-humidity equilibrium with the atmosphere inside the cabinet.

DISTENSIBILITY TESTING. Two strips measuring 1 x 6 inches were cut from each conditioned, free film. The strips were cut with a razor blade, using a steel template as a pattern. The thickness of these strips were then determined by averaging several readings taken with a dial gauge micrometer. A sample strip was then clamped between the jaws of the Scott testing machine and the load applied. The elongation of the film and the load required to break it were recorded, and from these measurements the percent elongation and the tensile strength of the film were determined.

EXTRACTION. The polymer content of the aged films was determined by extracting the film with acetone and considering the insoluble portion as polymer. A double thickness of #30 Whatman filter paper was folded into a double thickness, Whatman-extraction thimble. This thimble was then extracted with acetone for two days, permitting it to reach a constant weight. It was then dried at 106°C. for two hours, cooled in a dessicator, and weighed. The weighings were performed in a large weighing bottle on an analytical

balance. The film sample was cut into small bits (and ground in a mortar and pestle where possible), and approximately a gram and a half was placed in the thimble. The thimble was again dried, cooled, and weighed; the weight of sample was obtained by difference. The thimble, containing the sample, was then placed in an extraction unit and extracted for approximately two weeks to constant weight. An empty thimble was extracted with each ten samples as a blank, 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 percent of insoluble material remaining was calculated.

RESULTS.

The formulations, previously shown in Table I, were cast into films, and aged; and the elongation, tensile strength, and unextractable at failure determined. It was necessary to determine the length of a weathering cycle which would effectively bring about failure conditions in the film.

Typical samples were selected from the entire group (Table I) and the physical properties of these formulations were studied throughout the lives of their films. These experimental values were determined for the unaged films, as well as for films that had been aged for 2, 4, 6, 8, and 10 cycles. These results are given in Table II.

The results given in this table were calculated from the experimental measurements according to the following methods. The tensile strength was calculated by dividing the thickness of the film in inches, as measured by the micrometer, into the ultimate load in pounds required to break the film, as measured by the Scott tester. Since the film strips were cut one inch wide this calculation gave a tensile strength figure in pounds per square inch. The percent elongation of the films was determined by dividing the ultimate distance that a film elongates under load by the initial length of the film between the jaws of the testing machine. This fraction is multiplied by 100 to convert it to percent.

The determination of the percent unextractable necessitates a more complex calculation because it must be done on a volume basis, while the actual amount of unextractable material was determined by weight. In order to facilitate this calculation a formula was developed as follows:

To convert from weight to volume basis the weight factors must be divided by their respective specific gravities

$$\text{Volume \% unextractable} = \frac{\frac{W_{ux}}{G_{ux}} (100)}{\frac{W_f}{G_f}} = \frac{W_{ux} G_f (100)}{G_{ux} W_f} \quad (1)$$

where W_{ux} = weight of unextractable portion of film
 G_{ux} = specific gravity of unextractable portion
 W_f = weight of film sample
 G_f = specific gravity of film sample

The weight quantities in (1) are measured experimentally, but the specific gravities must be calculated by the formula of the enamel. For the film this quantity is calculated by dividing the weights of the individual constituents by their volumes

$$G_f = \frac{W_o + W_r + W_p}{V_o + V_r + V_p} \quad (2)$$

If it is assumed that all of the pigment is retained in the extraction thimble, making the specific gravity of the extractible material essentially equal to one, the following expression will represent the specific gravity of the insoluble phase

$$G_{ux} = \frac{(W_o + W_r + W_p) - \frac{W_{ex}}{1} (W_o + W_r + W_p)}{(V_o + V_r + V_p) - \frac{W_{ex}}{G_f} (W_o + W_r + W_p)} \quad (3)$$

where W_o = weight of oil in enamel sample
 W_r = weight of resin in enamel sample
 W_p = weight of pigment in enamel sample
 V_o = volume of oil in enamel sample
 V_r = volume of resin in enamel sample
 V_p = volume of pigment in enamel sample
 W_{ex} = weight of extractable material, experimentally determined

If equations (2) and (3) are substituted in (1), simplification of the resulting product gives the following simple formula

$$\text{Volume \% unextractable} = \left\{ 1 - \frac{(W_{ex})(W_o + W_r + W_p)}{(W_r)(V_o + V_r + V_p)} \right\} (100) \quad (5)$$

By the use of equation (5) the calculation of the percent unextractable by volume involves merely a straight-forward substitution.

The results shown in Table II are plotted in figures 6 to 11.

The volume percent unextractable is plotted against the age in cycles and the elongation in percent. These curves are very similar to those plotted by Ernst and Lubbers (4) for clear varnishes. It may be seen that for enamels as well as varnishes the polymer content increases relatively fast when the film is young, but approaches a constant value as aging continues. In all cases the value of the polymer content is essentially constant before the film has been aged ten cycles. It is also true that the values of the percent elongation of the enamel films decrease as the polymer content increases, reaching a minimum value as the value of the polymer content becomes constant. This is in agreement with the facts previously established (4).

TABLE II

Physical Properties of Typical Enamel Formulations at Varying Ages

Description of Sample	Physical Property	Age in Cycles					
		0	2	4	6	8	10
16 gallon linseed-Bakelite varnish with $\frac{1}{2}$ the resin replaced with TiO_2	% Unextractable	80.2	82.3	85.4	84.5	86.7	86.1
	% Elongation	65.2	17.5	5.2	6.2	8.1	6.8
	Tensile Strength	13	300	908	702	471	433
16 gallon tung-Bakelite varnish with $\frac{1}{2}$ the resin replaced with BCWL	% Unextractable	74.2	81.7	84.6	90.1	89.2	93.8
	% Elongation	***	10.2	2	1.5	.8	---
	Tensile Strength	***	585	834	1296	475	---
16 gallon linseed-ester gum varnish with $\frac{1}{2}$ the resin replaced with FeCrO_4	% Unextractable	77.5	79.6	83.7	81.8	84.7	84.1
	% Elongation			All films too fragile			
	Tensile Strength						
16 gallon linseed-ester gum varnish with $\frac{1}{2}$ the resin replaced with Fe_2O_3	% Unextractable	72.8	74.1	84.1	83.8	89.2	86.2
	% Elongation			All films too fragile			
	Tensile Strength						
33 gallon linseed-ester gum varnish with $\frac{1}{2}$ the resin replaced with TiO_2	% Unextractable	58.8	63.2	68.8	75.5	67.8	69.5
	% Elongation	67.3	17.3	59.5	18.1	21.1	14.4
	Tensile Strength	0	20	0	0	0	0
33 gallon linseed-Bakelite varnish with $\frac{1}{2}$ the resin replaced with BCWL	% Unextractable	75.9	76.6	82.7	79.0	85.3	83.0
	% Elongation	52.4	19.1	6.6	5.9	1.9	---
	Tensile Strength	105	330	843	1160	595	---

*** indicates that the film was too plastic to pull

--- indicates that the film was too brittle to pull

FIG. 6. VOLUME PERCENT UNEXTRACTABLE VS. AGE AND ELONGATION
FOR 16 GALLON LINSEED OIL-BAKELITE VARNISH WITH ONE-HALF THE
RESIN REPLACED BY TITANIUM DIOXIDE

FIG. 7. VOLUME PERCENT UNEXTRACTABLE VS. AGE AND ELONGATION
FOR 16 GALLON TUNG OIL-BAKELITE VARNISH WITH ONE-HALF THE
RESIN REPLACED BY BASIC LEAD CARBONATE

FIG. 8. VOLUME PERCENT UNEXTRACTABLE VS. AGE FOR 16
GALLON LINSEED OIL-ESTER GUM VARNISH WITH ONE-HALF
THE RESIN REPLACED BY LEAD CHROMATE

FIG. 9. VOLUME PERCENT UNEXTRACTABLE VS. AGE FOR 16 GALLON LINSEED OIL-ESTER GUM VARNISHES WITH ONE-HALF THE RESIN REPLACED BY IRON OXIDE

FIG. 10. VOLUME PERCENT UNEXTRACTABLE VS. AGE AND ELONGATION FOR 33 GALLON LINSEED OIL-ESTER GUM VARNISH WITH ONE-HALF THE RESIN REPLACED BY TITANIUM DIOXIDE

FIG. 11. VOLUME PERCENT UNEXTRACTABLE VS. AGE AND ELONGATION
FOR SS GALION LINSEED OIL-BAKELITE VARNISH WITH ONE-HALF THE
RESIN REPLACED BY BASIC LEAD CARBONATE

Since the values shown in the preceding curves for percent unextractable become essentially constant before the film has aged 10 cycles, it is safe to say that the polymer content of an enamel film at failure is essentially equal to the polymer content of the film at age 10 cycles. This is true even if visible failure has not occurred after the film had been aged 10 cycles, which was the more frequent case. A few of the films failed as early as 8 cycles, but most of them failed at 10 or more.

From these results it was concluded that failure conditions could be effectively obtained merely by aging the films for 10 cycles.

Now that the effect of pigments on the polymerization rate of some typical enamel films has been established, it remains to investigate the effect of varying amounts of pigment on the total polymer that has ultimately formed in a film when failure occurs. This was done by weathering films cast from the formulations shown in Table I. The weathering was carried on for 10 cycles at which time the films had approximated failure conditions. These films were elongated and extracted. From the experimental readings thus obtained the values of the percent unextractable, percent elongation, and tensile strength were calculated and recorded in Table III.

TABLE III

Physical Properties of All Films at Ten Cycles Age

Resin	Resin Volume	Pigment Volume	Pigment Volume	Percent Unextractable	Percent Elongation	Tensile Strength
<u>16 gallon linseed oil varnishes:</u>						
Bakelite	10	None	0	85	1.2	1500
Bakelite	5	TiO ₂	5	85	6.2	702
Bakelite	7	TiO ₂	3	74	5.5	700
Bakelite	9	TiO ₂	1	66	---	---
Bakelite	5	BCWL	5	79	1.1	211
Bakelite	7	BCWL	3	83	1.4	457
Bakelite	9	BCWL	1	90	1.6	473
Bakelite	5	PbCrO ₄	5	92	11.7	663
Bakelite	7	PbCrO ₄	3	83	3.1	577
Bakelite	9	PbCrO ₄	1	62	---	---
Bakelite	5	Fe ₂ O ₃	5	90	10.8	105
Bakelite	7	Fe ₂ O ₃	3	75	4.4	309
Bakelite	9	Fe ₂ O ₃	1	53	---	---
Bakelite	5	Cd yellow	5	87	6.9	768
Bakelite	7	Cd yellow	3	86	2.9	1111
Bakelite	9	Cd yellow	1	78	2.0	1067
Ester gum	10	None	0	61	---	---
Ester gum	5	TiO ₂	5	64	---	---
Ester gum	7	TiO ₂	3	76	---	---
Ester gum	9	TiO ₂	1	86	---	---
Ester gum	5	BCWL	5	92	---	---
Ester gum	7	BCWL	3	87	---	---
Ester gum	9	BCWL	1	80	---	---
Ester gum	5	PbCrO ₄	5	84	23.4	0
Ester gum	7	PbCrO ₄	3	85	---	---
Ester gum	9	PbCrO ₄	1	85	---	---
Ester gum	5	Fe ₂ O ₃	5	86	---	---
Ester gum	7	Fe ₂ O ₃	3	85	---	---
Ester gum	9	Fe ₂ O ₃	1	73	---	---

16 gallon castor oil varnishes:

Bakelite	10	None	0	92	2.2	2690
Bakelite	5	TiO ₂	5	93	9.7	1051
Bakelite	7	TiO ₂	3	90	8.7	1397
Bakelite	9	TiO ₂	1	89	4.2	1813
Bakelite	5	BCWL	5	94	2.3	1331
Bakelite	7	BCWL	3	90	10.1	2085
Bakelite	9	BCWL	1	92	2.6	1965

TABLE III (continued)

Physical Properties of All Films at Ten Cycles Age

Resin	Resin Volume	Pigment Volume	Pigment Volume	Percent Unextractable	Percent Elongation	Tensile Strength
<u>16 gallon tung oil varnishes:</u>						
Bakelite	10	None	0	88	1.6	500
Bakelite	8	TiO ₂	5	92	3.7	1060
Bakelite	7	TiO ₂	3	93	1.9	1240
Bakelite	9	TiO ₂	1	88	1.5	704
Bakelite	8	BCWL	5	90	2.2	834
Bakelite	7	BCWL	3	82	2.4	1049
Bakelite	9	BCWL	1	78	1.4	679
Bakelite	8	PbCrO ₄	5	91	1.8	787
Bakelite	7	PbCrO ₄	3	83	0.6	106
Bakelite	9	PbCrO ₄	1	79	1.2	260
Bakelite	8	Fe ₂ O ₃	5	88	5.3	1069
Bakelite	7	Fe ₂ O ₃	3	85	3.4	1291
Bakelite	9	Fe ₂ O ₃	1	78	0.3	168
<u>55 gallon linseed oil varnishes:</u>						
Bakelite	10	None	0	88	2.6	1775
Bakelite	8	TiO ₂	5	90	11.4	301
Bakelite	7	TiO ₂	3	90	11.9	732
Bakelite	9	TiO ₂	1	84	3.7	1260
Bakelite	8	BCWL	5	83	2.0	570
Bakelite	7	BCWL	3	88	1.6	1145
Bakelite	9	BCWL	1	90	3.5	1114
Ester gum	10	None	0	70	1.0	221
Ester gum	8	TiO ₂	5	68	21.1	0
Ester gum	7	TiO ₂	3	71	1.4	39
Ester gum	9	TiO ₂	1	75	0.5	23
Ester gum	8	BCWL	5	80	---	---
Ester gum	7	BCWL	3	73	---	---
Ester gum	9	BCWL	1	72	---	---

--- indicates that the film was too brittle to pull

The data in Table III include values for the percent unextractable at failure for clear varnishes and enamels having pigment-resin volume-ratios of 1/9, 3/7, and 5/5. This gives four samples which contain the same materials but have different pigment concentrations. The values of the polymer content at failure were plotted against the percentage of resin in the varnish replaced with pigment for each series of formulations. These curves are shown in figures 12 to 21.

On examination of these curves it is seen that in most cases pigmentation has a marked effect on the value of the polymer content of the varnish at failure, especially at low pigment concentrations.

Consider the linseed-ester gum enamels in both the 16 and 33 gallon oil lengths, figures 12 and 13. The effect of basic carbonate of white lead on the 16 gallon linseed-ester gum varnish is to cause the polymer content at failure to increase as the pigment concentration is increased. The effect is the same on the 33 gallon varnish but not so pronounced. Titanium dioxide causes a sharp rise in the failure polymer content of a 16 gallon linseed-ester gum varnish, when ten percent of the resin is replaced by pigment. The effect of additional pigment is to decrease successively the ultimate polymer until it is essentially equal to that of the clear varnish. This two-directional influence is also in force on 33 gallon varnishes, but to a lesser degree. The reason the

FIG. 12. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT RESIN
REPLACED BY PIGMENT FOR 16 GALLON LINSEED OIL-ESTER
GUM VARNISH

FIG. 13. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT
RESIN REPLACED BY PIGMENT FOR 55 GALLON LINSEED
OIL-ESTER GUM VARNISH

pigments have less influence on the 33 gallon varnish is that the resin-pigment portion of the film formed from a 33 gallon enamel occupies a much smaller fraction of the total film volume, than does the resin-pigment portion of a film formed from a 16 gallon enamel.

The results of figures 12 and 13 show that the substitution of basic lead carbonate in a varnish formulation brings about successive increases in the polymer content at failure. This could be due to a catalytic effect of basic lead carbonate to promote polymerization or to the formation of insoluble lead soap with the free acid in the oil or a coalition between the lead carbonate and the triglyceride radical. Lead chromate and iron oxide have the same effect but to a slightly lesser degree. That all three of these pigments are oil-reactive undoubtedly is a factor in this effect. Titanium dioxide in a small quantity caused the percent unextractable at failure of linseed-ester gum varnishes to be increased. When one-half the resin was replaced by inert titanium dioxide the polymer at failure was essentially equal to that of the clear varnish. This indicates that titanium dioxide can be substituted for resin in linseed-ester gum varnishes while the other pigments cannot be. The increases in polymer content at the lower pigment concentrations were due to the fact that the pigment was not present in amounts large enough to bring about a representative effect.

A comparison of these pigments on 16 and 33 gallon linseed-Bakelite varnishes is shown in figures 14 and 15. The effects appear to be rather varied, but much more pronounced on the 16 gallon varnish than on the 33 gallon varnish. The reason for this is the same as for the corresponding phenomenon concerning linseed-ester gum varnishes. Figures 14 and 15 reveal the fact that basic lead carbonate has a different effect than the other pigments on both the 16 and 33 gallon linseed-Bakelite varnishes. This effect constitutes a rise in the failure polymer content for samples in which ten percent of the resin was replaced by basic lead carbonate. This rise is followed by a subsequent decrease in this value as more pigment is added. This decrease will continue until the failure-polymer has become equal to that of the original clear varnish.

The effect of titanium dioxide in both the 16 and 33 gallon varnishes was to cause a decrease in the polymer content at failure of a sample in which ten percent of the resin was replaced with pigment. From this point an increase in the pigment concentration brought about an increase in this value to approximately the original value of the clear varnish. The other pigments incorporated in the 16 gallon varnish had the same effect as titanium dioxide. Cadmium sulfide did this to a lesser degree and iron oxide and lead chromate to a greater degree. The action of the lead on the

FIG. 14. VOLUME PERCENT UNEXTRACTABLE VS.
PERCENT RESIN REPLACED BY PIGMENT FOR 16 GALLON
LINSEED OIL-BARELITE VARNISH

FIG. 15. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT
RESIN REPLACED BY PIGMENT FOR 33 GALLON
LINSEED OIL-BAKELITE VARNISH

linseed-Bakelite varnishes may be justified on the basis that a partially soluble compound is formed which tends to catalyze the polymerization of the varnish. When the concentration of lead is increased beyond a certain point the solubility effect of this compound overshadows its catalytic effect. The net result is a decrease in the amount of insoluble material at failure. The action of the remaining pigments seems to be a combination of a negative catalytic effect and a bulking effect as the pigment concentration increases. That is, the pigment in small amounts (10% of resin-pigment volume) decreases the amount of unextractable material at failure because the pigments hinder the polymerization of the oil with the resin. As more pigment is added, which is positively an insoluble phase, this negative effect is overcome by the increase in bulk of insoluble pigment. Finally, it is evident that no matter what the intermediate effects are, the pigments investigated may be substituted for resin in linseed-Bakelite varnishes. This substitution will bring about virtually no change in the polymer content at failure as long as fifty percent of the resin is replaced by pigment.

The action of lead carbonate and titanium dioxide on 16 gallon castor oil varnishes, as shown by figure 16, was small, even at low pigment concentration. In fact, the curves for these enamels are practically straight lines within the limit of experimental error. It is postulated that the pigment influence on

FIG. 16. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT
RESIN REPLACED BY PIGMENT FOR 16 GALLON CASTOR
OIL-BAKELITE VARNISH

53 gallon castor oil varnishes would be even less. It follows that resin may be replaced by pigment up to amounts of fifty percent at least, in castor oil-Bakelite varnishes.

According to figure 17 the action of titanium dioxide on 16 gallon tung-Bakelite varnish is characterized by an increase in the polymer content at failure for increasing additions of the pigment. The reactive iron oxide, chrome yellow, and lead carbonate give an initial decrease to this figure, followed by subsequent increases as more pigment is added. This effect may be due to the catalytic or autocatalytic formation of soluble compounds, the effect of which is overcome by the addition of insoluble bulk afforded by increased amounts of pigment. The titanium dioxide, being non-reactive, serves merely to increase the bulk of insoluble material. Although these initial effects are varied, the ultimate value of the polymer content, when one-half the resin is replaced by any of the above pigments, is equal to that obtained for the clear varnish.

Figure 18 illustrates the effect of titanium dioxide pigment on the different vehicles that were used. Figures 19, 20, and 21 show the same thing for basic lead carbonate, lead chromate, and iron oxide, respectively. The curves for the lead chromate and iron oxide pigments of the same general shape, regardless of the vehicle. For titanium dioxide and basic lead carbonate the

FIG. 17. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT
RESIN REPLACED BY PIGMENT FOR 16 GALLON TUNG
OIL-BAKELITE VARNISH

FIG. 18. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT
 RESIN REPLACED BY TITANIUM DIOXIDE

FIG. 19. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT RESIN REPLACED BY BASIC LEAD CARBONATE

FIG. 20. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT
RESIN REPLACED BY LEAD CHROMATE

FIG. 21. VOLUME PERCENT UNEXTRACTABLE VS. PERCENT
RESIN REPLACED BY IRON OXIDE

effects are quite varied.

In comparing the percent elongation and tensile strength values of the enamels with those obtained for the clear varnishes, the following general effects are noted. In all cases except for the 16 gallon tung-Bakelite series, the tensile strength of the enamel films are less than that of the clear varnishes. In every case the percent elongation of the enamel films at 10 cycles age was greater than that of the clear varnishes.

From these observations it seems that the polymer networks of the enamel films are interlinked with less complexity and therefore are less rigid than the corresponding varnish films. This fact indicates that the enamel films are more easily able to adjust themselves to the internal and external stresses that take place in a film during aging; consequently they have longer life. On the other hand, the varnish films are more resistant to any molecular rearrangement than the corresponding enamel films, as indicated from the tensile strength data.

CONCLUSIONS
AND
RECOMMENDATIONS

The results of this research were coordinated with those of the preceding investigations to form the following conclusions:

(1) The pigments that were investigated affected the polymerization rate of the varnishes only to a small extent.

(2) When the pigments were substituted for resin in amounts less than fifty percent the polymer content at failure was either increased or decreased. When made for ester gum, the substitution brought about increases in the failure-polymer in all cases. When made for Bakelite resin, the substitution of pigment brought about a decrease in the polymer content at failure with two exceptions. These exceptions are titanium dioxide in tung oil varnishes and basic lead carbonate in linseed oil varnishes.

(3) The magnitude of these variations that occur when pigment is substituted for resin in amounts less than fifty percent is dependent on the drying oil used in a varnish and its oil length. The variations were greatest for linseed oil, smaller for tung oil, and smallest for castor oil. They were smaller in the longer oil varnishes.

(4) When fifty percent of the resin is replaced by pigment, the results may be generally classified as follows. In Bakelite varnishes (typical of insoluble type resin) the substitution can be made with effectively no change in the polymer content at

failure. In ester gum varnishes (typical of soluble type resin) only inert titanium dioxide may be substituted without effect. The result of substituting the reactive pigments is to increase the polymer content at failure into the range of the insoluble resin type varnishes and enamels.

(5) The flocculating tendency of cadmium yellow pigment exhibited no distinguishing characteristic in its action on oleoresinous film structure. The effect of its substitution in the formulations was similar to that of the other pigments.

(6) The pigments studied caused a decrease in the tensile strength (except in the case of the tung-Bakelite varnishes) accompanied by an increase in the percent elongation of the varnish films. This latter observation correlates the fact that enamel films are more durable than clear varnish films.

For the continuance of research in this field the following recommendations are made for future work.

Some of the enamels studied this year should be overloaded with pigment, even to the point of replacing one-hundred percent of the resin with pigment. On the other hand, samples containing small amounts of pigment (less than ten percent) should be analyzed. These results would serve to extend the 'polymer content at failure vs. percent resin replaced by pigment' curves out beyond fifty percent and would also investigate the large changes that take place

in the curves between the varnish films and the slightly pigmented enamel films.

Additional work should include the replacement of resin with synthetic, chemically manufactured organic pigments. As a starting point one pigment should be chosen from each of the five classes of synthetic pigments outlined by Mattiello (17). These five groups are basic, insoluble azo, soluble azo, condensation acid, anthraquinone and vat. These pigments should be incorporated in the varnishes in varying amounts and their effect on the structure of the resultant films studied.

Some work in the field of baking enamels with infra-red drying as one of the variables might also prove interesting and informative.

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V I T A

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