

# *When to Varnish*

*How long should an oil painting  
dry before varnishing?*



By

Artist and Chemist

Chuck Mauldin

First published on-line  
by Rocking M Ventures LLC at

[www.WhenToVarnish.com](http://www.WhenToVarnish.com)

October 2012

*Dedicated to all artists  
who strive to be  
the very best they can be.*

DISCLAIMER

The use of the information contained in this report shall be at the reader's risk and solely at the discretion of the reader. Rocking M Ventures LLC and Chuck Mauldin make no warranties, representations, or guarantees in connection with the information in this report. Under no circumstances is Rocking M Ventures LLC or Chuck Mauldin liable for any costs, direct or incidental, or consequential damages resulting from any use or application of the information contained in this report.

# Table of Contents

	<u>Page</u>
Chapter 1 Overview	4
Chapter 2 State of the “Chemistry Art”	
Linseed Oil	5
Varnishes	10
Chapter 3 Experimental Search for Answers	
Changes with Time of Linseed Oils and Paints	13
Swab Tests of Paintings	17
Chapter 4 Conclusions	23
Biography	25
Appendix A Summary of Experiments	26

# Chapter 1 Overview

How long should an oil painting dry before varnishing? Six to twelve months? Sounds like a prison sentence, and it is when imposed on a new born oil painting! But that's the range of time recommended on most varnish labels for allowing an oil painting to dry before varnishing. However, faced with deadlines of competitions, gallery shows, commissions, and heightened by the excitement of getting that new painting to market, artists often choose to compromise on this recommendation. We varnish early, or not at all, or maybe apply retouch varnish as a stopgap, perhaps with some sense of guilt, concern, or confusion regarding this final step in preparing a painting for longevity. It is amazing that, with all of the excellent information available about painting, rarely is the topic of when to varnish even discussed. Such an important topic, yet little is truly established.

One thing is clear. Everyone wants their paint layer to be properly cured to a strong, durable, insoluble film. That is expected and will not be compromised. Most also want to apply a varnish to their oil painting in order to (1) protect it from dirt and grime with a *removable* outer layer and (2) provide an attractive, uniform finish. It's the final step in creating a professional looking, built-to-last work of art. Unfortunately, these dual desires of properly cured and varnished can seem hard to satisfy when a six month waiting period is enforced.

The frustration is further aggravated by the lack of reasons or explanations as to why such prolonged drying is needed. Nothing definitive is stated technically, much less supported by scientific evidence, in reference books, how-to books, magazine articles, or the web. There is an assumption that the varnish can adversely affect the curing process in some way. For example, some have claimed that varnish may block the oxygen needed to harden the paint. Others have warned of premature cracking. However, a full explanation and supporting data are strangely absent.

Fifteen years ago, I embarked on an effort to answer the question of "How long should an oil painting dry before varnishing?" Part of this quest involved reviewing some of the available technical literature concerning the curing and aging of oil paint. Chapter 2 is devoted to making an artist-friendly, simplified summary of this complex, voluminous information. With this as crucial background, a variety of simple experiments are described in Chapter 3. Most importantly, the implications of my experiments for varnishing are discussed in Chapter 4.

And the answer? At least three weeks (of course, that depends on many factors, like the presence of driers, mediums, and the thickness of the paint, to name a few). No reason to wait six to twelve months was found. Bottom line: if it's dry enough to varnish, it's dry enough to varnish! That's my opinion, not my recommendation. The latter implies liability. So, please read my evidence and decide for yourself.

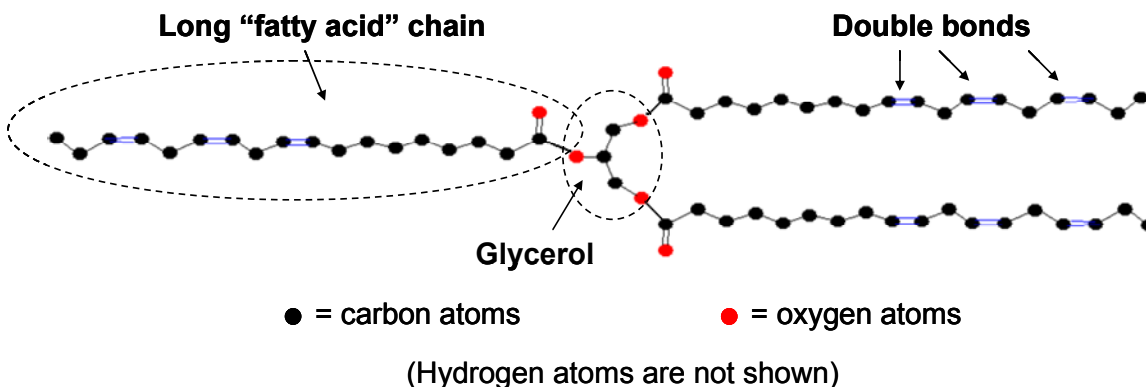
## Chapter 2 State of the “Chemistry Art”

### Linseed Oil

The chemistry of drying oils (like linseed oil) and the paint derived from them has been the subject of an enormous amount of research over the past century. Even for a chemist like me with 36 years of experience, it can be overwhelming. Fortunately, a recent PhD thesis, only ten years old and available on the web, provides a very thorough, well written summary of the state of the art, especially concerning linseed oil and linseed oil based artists’ paint. (It also documents some intriguing, ground breaking new results on paint aging, which will be discussed later in this Chapter). The thesis is written by Jorrit Dirk Jan van den Berg and is entitled “Analytical chemical studies on traditional linseed oil paints.” His research was sponsored by MOLART – Molecular Aspects of Aging of Painted Art, an extensive cooperative project between art restorers, chemists, and physicists funded by the Dutch Organization for Scientific Research from 1995 to 2003. Essentially all of the chemistry discussed below is based on detailed information found in van den Berg’s Chapter 2. More recent publications have been reviewed, but their contributions appear consistent with the information reviewed by van den Berg.

In order to meet my goal of providing an “artist-friendly” description of linseed oil chemistry, many gross simplifications will be made! We will avoid getting bogged down with all the versions of linseed oil, like cold pressed, refined, boiled, etc, and the role of mediums and driers. These topics are important, but the simplified, overarching chemistry will apply to all. So, with apologies to the scientific community, the discussion will try to focus on the key aspects of the chemistry that could be impacted by varnishing.

Linseed oil consists of *three* long carbon chains (fatty acids) attached to a central glycerol core, as shown in the diagram below. Note that the chains are not rigid - they can easily curl up and flop around – at least in the liquid state. Also the molecule is three dimensional, not really flattened out like drawn here.



Glycerol is three carbons long with an oxygen attached to each carbon. These oxygens form bonds with the fatty acid chains. This connection between the fatty acid and the glycerol is called an “ester.”

There are several fatty acids chains possible, depending on length and the number of carbon-carbon “double bonds” present. The most common one in linseed oil contains a chain of 18 carbon atoms and three double bonds, like shown above. These double bonds are critically important! They are much more reactive than single bonds, and here, are the source of the reactions that lead to the transformation of the liquid to the solid.

When artist’s oil paint is spread out over a surface and exposed to air, the linseed oil in the paint begins a life-long sequence of chemical processes – some good and some bad. It is helpful to separate the chemistry into the steps of (1) curing, followed by (2) aging. Curing refers to the transformation of the linseed oil from a viscous liquid to a flexible solid (commonly referred to as drying). Aging then refers to the changes that occur to the solid, typically over a prolonged period of time (many years).

The curing and aging processes are illustrated in the diagram on the next page. The diagram represents only one of the many, many possible structures that can form during curing and aging. It does, however, serve to illustrate the main kinds of reaction products that are known to form.

## **Curing**

In the curing process, the changes are primarily caused by the reactions of oxygen (in the air) with the long chains, who are willing partners because of the presence of those double bonds. This oxidation reaction is called autoxidation and, in this case, does two main things:

(1) It adds oxygen to the chain. At first, the new oxygen is in the form of a “hydroperoxide,” which is what is shown on the diagram. Hydroperoxides tend to undergo further reactions, which we will cover under aging. Oxygen addition causes the oil to gain weight. The cured structure in the diagram corresponds to a weight gain of 7.3%, which is similar to the experimental gains in Chapter 3.

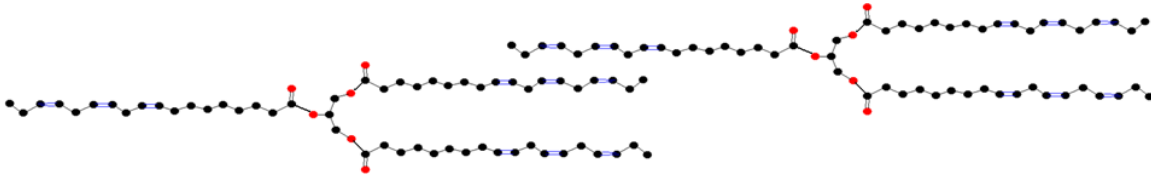
(2) It generates new bonds between chains. This new bond formation is called “cross-linking” and is the single most important thing that happens *during* the oxidation reactions – it is the main reason the oil changes from liquid to solid. The new bond shown in the diagram is a bond between carbons. New cross-linking bonds involving oxygen are also known to occur. This single connection between two linseed oil molecules starts the solidification process. Cross-linking to additional linseed oil molecules generates the polymeric form of cured linseed oil. Pretty amazing!

## The Curing and Aging of Linseed Oil

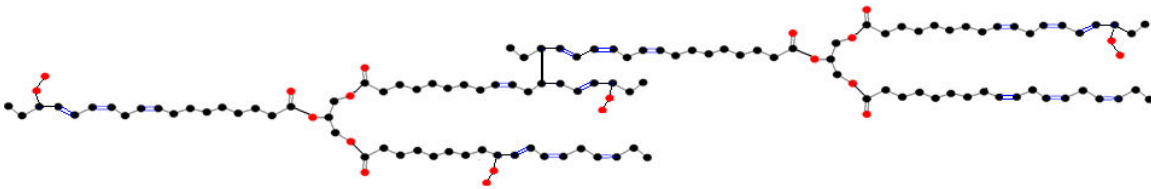
● = carbon atoms

● = oxygen atoms

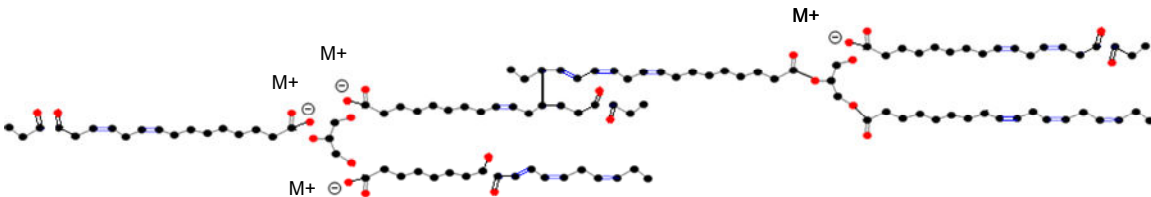
(Hydrogen atoms are not shown)



(a) STARTING OIL. Two linseed oil molecules shown.



(b) CURED. After reaction with O<sub>2</sub> and formation of a cross-linking bond.



(c) AGED. Formation of volatile fragments and breakup of the esters.

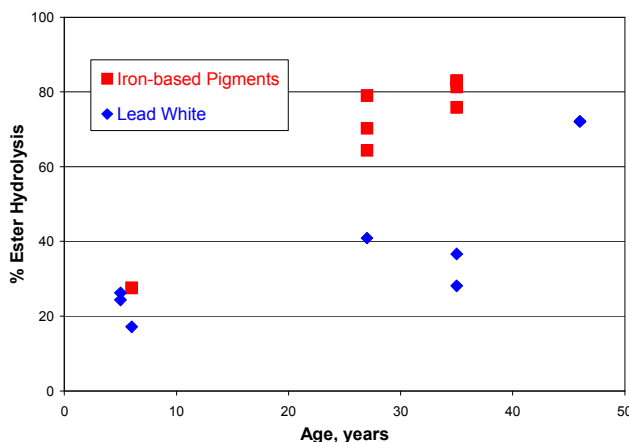
For a painting made with straight tube colors (no driers) and kept under typical room conditions, the oxidation reactions are relatively slow, taking 5-10 days at least. One of the reasons for the slow rate is that the reactions can be limited by the diffusion of oxygen into the paint film. Exposure to light and the addition of driers help start the oxidation reactions. Temperature also helps speed things up, as artists working plein air during a hot summer can attest. Storage of the palette in the refrigerator, as some artists do, helps slow things down.

## Aging

The point when curing is over and aging begins is not a distinct step because the chemistry assigned to the two stages can overlap. As will be apparent in experiments discussed in Chapter 3, oxygen can continue to be incorporated into the oil, reacting the same way as in curing, although at a much slower rate. However, other reactions take over after the initial oxidation. Two in particular are the formation of volatile material and the breakup of the esters.

Volatile material refers to compounds that can evaporate off of the oil painting. They are made from the oxidized fatty acid chains (from the hydroperoxides). An example of one of the more prevalent volatile compounds that is made is propanal, which contains three carbons and an oxygen. These small, unattached fragments are shown in the aging portion of the diagram. Molecules like this may take some time to evaporate off of a painting, because they are formed within the solid framework of the cured linseed oil – they're trapped. When/if they do come off, a weight loss will occur, which may or may not be observed because, recall, the oxidation reactions are causing a weight gain. Just how this works out will be addressed in Chapter 3. Several other oxidized compounds are formed besides propanal, depending upon where the hydroperoxides are along the chains. Overall, this fragmentation of the cured linseed oil is not good, because if a lot of fragments are formed and leave, the remaining linseed oil film will want to shrink, which could cause a paint layer to crack.

A second major change that occurs much more slowly during aging is the breakdown of the ester groups present in the original linseed oil – elimination of those special connections between the fatty acid chains and the glycerol core. As demonstrated by outstanding analytical work on aged paintings by van den Berg and described in Chapter 5 of his thesis, esters are gradually decomposed over a prolonged period of time. The reaction is called ester hydrolysis and is very well known in chemistry. The new finding here is that it is occurring to a major extent on old oil paintings. The figure below, based on van den Berg's data, shows the increase in ester decomposition with age. Decomposition levels as high as 80% are reached after thirty five years. In the aging diagram, 4 out of 6 ester groups (67%) are shown broken to illustrate the idea.



↩ Figure prepared from data in van den Berg's thesis, Chapter 6, Tables 3 and 4.

Iron-based Pigments and Lead White refer to the types of oil paint sampled on the paintings and then analyzed. The finding that pigment type affects ester hydrolysis is surprising and not well understood.



Ester hydrolysis requires water, not oxygen, and occurs by the following general chemical equation:



The products are a carboxylic acid and an alcohol. According to van den Berg, the carboxylic acids are mainly present as metal carboxylate salts. In other words, the acids are in their negatively charged form (shown with a circled “minus” on the diagram). This charge is balanced by a metal ion,  $\text{M}^+$ , which the free acid extracts from virtually any of the metal-containing pigments we all use (like iron, cobalt, cadmium, titanium, etc):



Formula for a metal carboxylate

The important concept developed by van den Berg is the irreversible transformation of the original “purely organic polymer” present in cured linseed oil into an “ionic-compound-containing polymer (called an ionomer).” This change has significant impacts. It is responsible for the oil painting becoming increasingly harder with time, more prone to cracking, and less soluble in organic solvents. It is a rather drastic change in the nature of the linseed oil; a change that has nothing to do with oxygen availability.

In summary, linseed oil undergoes significant changes as it cures and ages. The presence of the many double bonds in the fatty acid chains enables easy reactions with oxygen in the air. These reactions are sufficient to generate bonding between linseed oil molecules, which transforms the viscous liquid into a strong, flexible solid. However, the oxidation reactions are accompanied by fragmentation of fatty acid chains, which can lead to the loss of mass and weakening of the solid. Ultimately, the cured linseed oil is further changed by the action of water, breaking down the esters into metal carboxylates, which remain part of the paint layer. Overall, it is a chemically complex system that functions amazingly well, considering the long history of oil painting and the many preserved examples present in collections and museums today.

## Varnishes

A large amount of scientific work has been done on varnishes, much like for linseed oil. However, for the purposes of this report, we can avoid all but the simplest aspects of the chemistry, and focus on the main features of today's most commonly used varnishes for oil paintings.

The main, important difference between linseed oil and the varnish is that linseed oil is reactive, undergoing significant chemical changes as discussed above, whereas the varnish is non-reactive. There are no chemical changes upon drying, only evaporation of the solvents. There can be, however, very long term changes to the varnish caused by slow oxidation reactions, but those changes are not that relevant to the present discussion.

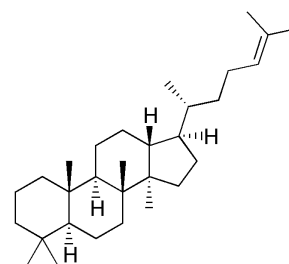
A varnish is applied to a painting for the following reasons:

- It provides a uniform sheen to the work, eliminating the range of shiny to dull areas that typically occur.
- It protects the oil paint surface from air-borne pollutants, like dirt, acidic compounds, sulfur compounds, mold, and the like.
- It enables restoration by being removable with a solvent.
- It is the final, professional step for preparing the painting for the future.

Varnishing is the artist's final creative touch. The degree of gloss, for example, will be at the sole discretion of the artist. Collectors, who may not know about varnishing, rely on the artist to properly preserve their painting.

There are several types of varnishes for oil paintings, the two most common being dammar and acrylic-based synthetics. Both types are quite acceptable - the choice of which to use is up to the artist. The only way to really decide which varnish you like is to try them.

Dammar (also spelled damar) is a naturally occurring "triterpenoid" resin that is applied as a solution in a volatile solvent, such as turpentine. It is popular because it has been in use for a long time and provides the degree of gloss desired by many artists. It is chemically complex as expected for a natural product, and susceptible to contamination depending on the care taken in making the varnish. Studies of long term aging show the same general types of reactions that occur with linseed oil, namely oxidation, formation of volatile products, and even some cross-linking.



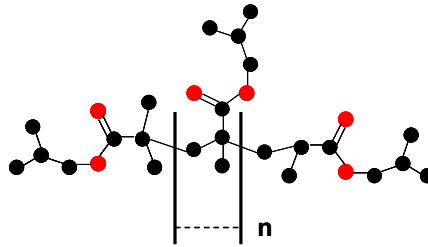
Dammarene  
An example of a triterpenoid

The acrylic-based synthetics, such as Liquitex Soluvar and Golden MSA, consist of a colloidal suspension of one or more of polymerized methacrylates in various volatile solvents. The exact compositions are proprietary. Synthetic poly(methacrylates) are relatively pure and not as complex chemically as dammar. The key feature of these varnishes, as advertised, is their ability to be more easily removed than dammar. Most are available in matte and gloss formulations. More recent versions also contain a UV light stabilizer, which protects the varnish from long term oxidation. Less is known about aging compared to dammar, but most claims suggest good long term stability.

My personal choice is Liquitex Soluvar, which is poly(isobutyl methacrylate) in a volatile solvent. A mixture of 4 parts by volume of gloss to 1 part of matte imparts the right amount of gloss to the painting for my taste. This mixture is easily made by combining a 32 oz. container of gloss with an 8 oz. bottle of matte, using a clean milk jug (shaking vigorously). Pour the mixture back into the original containers, and label them "4G" for "4-parts gloss." I apply one, medium coat with a soft 2 inch brush, typically to a group of paintings which will have various ages. I have used Soluvar for over 20 years with no problems, no yellowing, no cracking, only great looking paintings! (ha!).

#### Poly(isobutyl methacrylate)

n = a large number of repeating units



● = carbon atoms

● = oxygen atoms

(Hydrogen atoms are not shown)

Another interesting, newer varnish is Gamblin's GAMVAR. It's also a synthetic, a polymer made from urea, formaldehyde, and 2-methylpropanal. The polymer is in a "low molecular weight" form which means the polymer strands are not very long. This enables the varnish to be removable. GAMVAR comes in a kit containing the polymer solid and a solvent, so the varnish can be freshly mixed (apparently to protect the UV stabilizer). According to Gamblin, the gloss can be attenuated by addition of Gamblin Cold Wax Medium. Most interesting, Gamblin states, "While waiting 3 – 6 months is best, painters using GAMVAR can *safely varnish sooner* because GAMVAR's mild solvent will not dissolve the glaze layers of paintings and *paintings today dry quicker*" (my italics!).

All of these varnishes are good choices. They will do their job as soon as they are given the chance. They have been accused of being a barrier to oxygen diffusion, but I could find no evidence to support that. In fact, oxygen permeability would be expected to be on the same order for isobutyl

methacrylate as for cured linseed oil – both are oxygenated organic polymers, with similar oxygen solubilities and capillary pore structures. And, as anyone knows who has varnished a painting, the varnish layer is pretty thin after the solvent evaporates.

A suggestion some have made regarding the problem of waiting 6 months to varnish, is to apply retouch varnish as soon as the surface is dry as a temporary stop-gap. There seems to be an assumption that retouch is ok but full varnish is not, which is rather curious since retouch varnish is simply diluted dammar. Apply enough retouch and you've varnished the painting – which is what should be done!

A comment on varnishing with liquin: It is shocking how many top-level professional artists are using liquin as a varnish. They apparently like the degree of gloss. This is terrible! Liquin is not a varnish. It is a drying oil – an alkyd, a faster drying cousin of linseed oil. It will eventually age like linseed oil, shrink and crack because there's no pigment present, turn yellow, and, the worst part, never be removable. There is no conceivable reason to varnish with liquin when there are so many good alternatives – like *real* varnishes.

We have focused on the varnishing of traditional oil paintings in this report. However, varnish can and should be applied to acrylic paintings as well. With acrylics, there are no chemistry issues involved in drying. They simply lose their water solvent and are then ready for varnishing. As with oils, the varnish provides a removable, protective layer and a uniform sheen.

Likewise, paintings made with water-soluble oil paint should be varnished just like regular oil paintings. Water-soluble oil paints, now made by several manufacturers, were first patented by inventors at Grumbacher (US patent 5,312,482, issued May 17, 1994). These paints contain the normal drying oils like linseed oil and, hence, undergo all the same curing and aging chemistry as traditional oil paint. The water solubility comes from the presence of about 5% of a special soap (a soap is a long organic molecule that likes oil, except for its one "ionic" end which likes water). This special soap is made with the same type of fatty acids that are present in linseed oil, with the acid neutralized with an organic base (an amine). On the one hand, it behaves just like a normal soap – making the oil in the paint "soluble" in water (actually forming an emulsion). On the other hand, because of those double bonds along the fatty acid chains, it behaves just like linseed oil – participating in the oxidation reactions and the all-important cross-linking. So the soap ultimately ends up bound in the paint film. Very clever! And very useful for those artists who like the properties of oil paint but need, or prefer, to use water as their solvent.

## Chapter 3 Experimental Search for Answers

Despite the enormous amount of research into the chemistry of linseed oil with increasingly more sophisticated methods, questions remain. One, the subject of this report, is “How long should an oil painting dry before varnishing?” As far as I am aware, there is no definitive answer in the available technical literature. The topic is just as ignored in the chemistry world as it is in the art world.

Presumably the varnish manufacturers know something, but they aren't sharing much for proprietary, competitive reasons. Where they came up with the six-to-twelve month recommendation for drying before varnishing is a mystery. It is suggested in Mayer's The Artist's Handbook of Materials and Techniques (5<sup>th</sup> Ed, page 209) that it is a holdover from the past when thick varnish layers were common. No doubt the companies are more interested in minimizing *their* liability risk than in minimizing *your* waiting time and have elected to err on the side of ultraconservatism. After all, it is hard to imagine a painting – no matter how thickly it is painted - that is not 100% cured by 6 months. But, as working artists, we deserve a better explanation.

So, starting about fifteen years ago, I began to conduct very simple in-home experiments in an effort to try to find some answers. Even though the most routine analytical methods were unavailable, relevant results were obtained and are the subject of this chapter.

Different types of experiments were pursued. Weight changes were measured over time - over four years in some cases - using small aluminum pans containing either linseed oil or straight-from-the-tube paint. Weight changes were also measured on cylinders of painted canvas. Actual paintings, some varnished, some not, ranging in age out to twenty years, were investigated with a cotton swab test. The swab test was also used to analyze a test canvas that had portions varnished after various drying times. These experiments will be reviewed in this chapter. More details are provided in Appendix A.

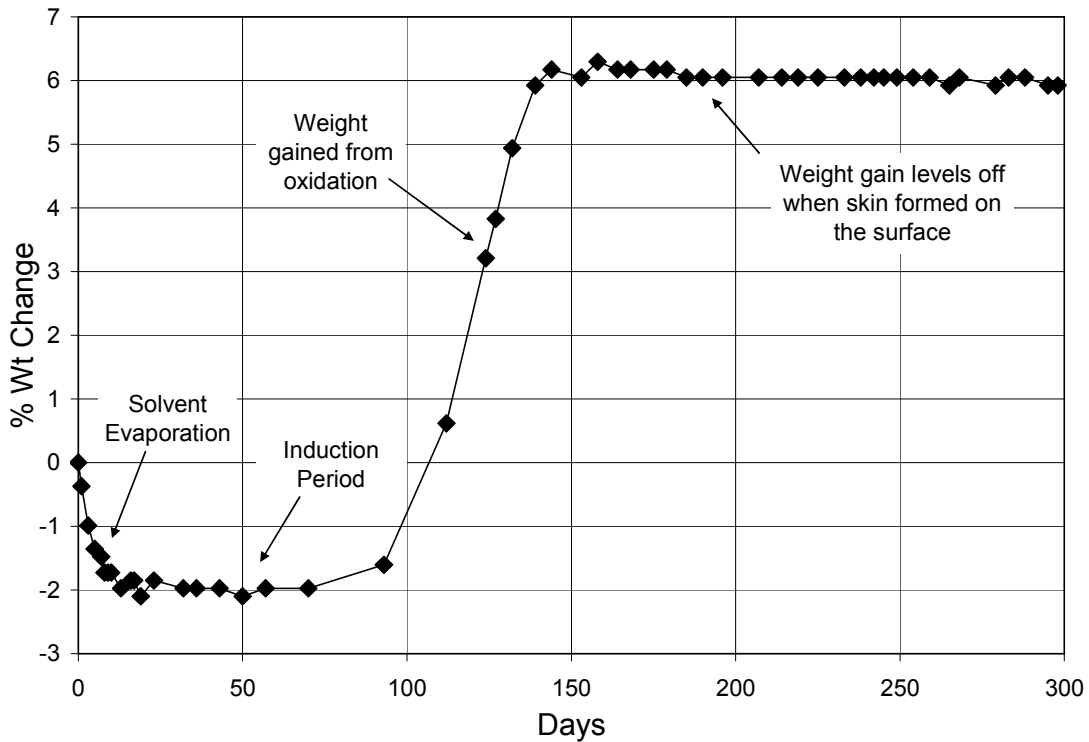
### Changes with Time of Linseed Oils and Paints

Measuring weight changes in linseed oils is a throw-back to the 1920's! However, even back then, rarely did the measurers take the time - or have the time - to do their experiments at room conditions, i.e. the conditions most relevant to oil paintings. Higher temperatures were commonly used to speed up the chemistry. This drawback was not a factor here. Changes in weight were allowed to occur naturally – with temperatures reflecting normal indoor conditions (except for a few experiments at 90 F). The linseed oils were poured into 2.5 inch diameter aluminum pans and allowed to stand, with a clear glass cover suspended above to protect from dust but positioned to allow normal air circulation and exposure to normal room light.

Figure 3-1 shows the changes in weight observed for a pan test of Gamblin refined linseed oil (1/8 inch deep) at room temperature. After an initial loss of about 2%, which is the evaporation of a solvent, constant weight is observed for the next 60 days. Then, finally, a gain in weight begins.

Once the reaction starts, weight increases with a slow, but steady rate. Then, rather suddenly, the gain in weight ceases. This stoppage is accompanied by the very obvious formation of a skin on top of the oil. This relationship was consistently observed. The simple explanation is that the main oxidation reaction “stops” (actually slows to a crawl) when the diffusion of oxygen is drastically reduced by the polymerization of the oil surface. The total amount of weight gained (starting from day 19) during this initial oxidation in this test is 8.4%.

Figure 3-1  
Weight Changes of Refined Linseed Oil



The long induction period seen here is not unusual for autoxidation reactions. Really long inductions were often observed for pure linseed oils, but were not seen in tests with paint (see Appendix A). Hence, the presence of a pigment helps get the oxidation reaction started.

Figure 3-2  
Weight Changes of Boiled Linseed Oil

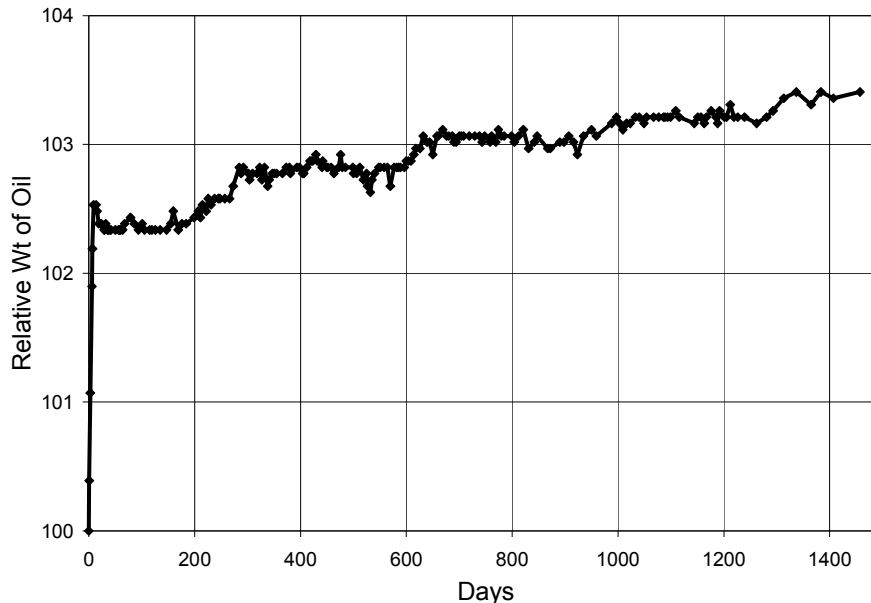


Figure 3-2 shows the results from a much longer test, made with a boiled linseed oil from Houston Art & Frame Co. Here the oil underwent an immediate weight gain that leveled off at about 2.5%. The lack of an induction period is believed to result from the oil already being significantly oxidized by the boiling processing and the likely presence of a drier. The 2.5% gain, compared to the 6-8% seen with the Gamblin refined oils, is also consistent with this oil being “pre-oxidized.” After the initial increase, weight continues to rise, showing an additional 1% gain over the 1400 day period (4 years). Interestingly, this small, long term weight gain was obtained in spurts. There were periods of gain, then periods of no gain. The pattern is an annual one, with the gains occurring during the summer and the no-gains occurring during the winter. Seasonal changes in humidity, and perhaps seasonal changes in room temperature, are felt to be the root cause of this “wiggle” to the overall pattern of gain.

Besides the changes in weight, the linseed oils underwent changes in appearance. After formation of a rough textured skin, which always signaled the end of the initial weight gain, samples developed a pronounced “wrinkly” appearance, with mountains and deep valleys, as shown in this photo of the Boiled Linseed Oil at day 1400. These contortions are caused by the cross-linking that has solidified the oil. The surface of the cured, polymerized linseed oil is dry to the touch but quite flexible. It feels like rubber. Thicker samples may have some liquid left beneath a surface layer. The dark amber color here was unique to the boiled oil; all other samples were straw-colored.



From the appearance, the cured oils look like they have shrunk in volume. Several attempts were made to measure changes in volume, but the results were unreliable, showing 20-35% shrinkage, which corresponds to unrealistic densities of 1.2-1.5 g/cc. The density of a cut-out piece of one sample (Gamblin Refined Linseed Oil at day 225, 1/8 inch deep), measured directly by water displacement was 1.01 g/cc, which corresponds to a volume shrinkage of about 8%. Similar volume shrinkages were reported by Svane (Surface Coatings International Part B: Coatings Transactions Vol.89, Issue B4, 2006, published by Oil & Colour Chemists' Association).

This wrinkling and shrinkage seen with the oil by itself were not seen in tests with paint. The presence of pigment particles must negate the structural stresses generated by the polymeric state of the oil.

Weight changes were measured in a number of other experiments. These included tests of different linseed oils at various depths and at 90 F and tests of paint, as bulk samples in pans and as thin and thick layers on canvas. The results reinforce the findings discussed above, typically showing initial weight gains followed by much slower gains. Interestingly, the tests of linseed oils at the higher temperature showed shorter induction periods and faster rates of oxidation, as expected, but not higher levels of weight gain. Again, the formation of a surface skin shut down the oxidation. This skin forms when the oxidation reaches a certain point, independent of temperature. Pan tests with real paint were consistent with the linseed oil tests. The painted canvases showed initial weight gains, as expected, but long term changes proved difficult to quantify. Graphs of the data and more discussion are provided in Appendix A.

## **Summary and Conclusions**

All of the experiments measuring weight changes are summarized in the table on the next page. Initial gains ranged from roughly 5 to 8%. Painted canvases, with 70 and 200 micron thicknesses, were in this range as well as oil and paint tests with much thicker depths.

As mentioned in Chapter 2, changes in weight can be difficult to interpret because of the possibility of having weight gain (O<sub>2</sub> addition) occur simultaneously with weight loss (volatile compounds). However, all but one of the experimental tests conducted here show a net long term gain. If losses are being masked by the gain, they must be smaller by comparison. It is reasonable to conclude that, in these room temperature experiments, the volatile products have tended to remain trapped within the polymerized oil.

Overall, the tests show remarkable consistency, with a range of about 5-8% gain initially, which is consistent with a fair amount of oxygen incorporation. The most important conclusion derived from these results is that, in most cases, most of the weight that is gained comes from the initial gain. As soon as there is sufficient polymerization to generate a surface skin, weight gain slows drastically.



Another key point is the absence of any meaningful weight change in any experiment that would indicate some significance to the 6-12 month period (the suppliers' recommended waiting time for varnishing). There isn't much happening before or after this point in time; nothing to suggest that an important turning point in curing is being reached then.

### Summary of Weight Changes Observed

Experiment	% Weight Change			
	Initial	At day	Final	At day
Gamblin Refined LO, 1/8" deep	<b>8.2 *</b>	144	<b>8.0 *</b>	300
Gamblin Refined LO, 1/4" deep	<b>7.2 *</b>	168	<b>7.1 *</b>	300
Gamblin Refined LO, 3/8" deep	<b>6.8 *</b>	179	<b>6.8 *</b>	300
Gamblin Cold Pressed LO, 1/8"	<b>7.4</b>	219	<b>7.4</b>	300
Gamblin Cold Pressed LO, 1/4"	<b>6.5</b>	279	<b>6.5</b>	300
Gamblin Cold Pressed LO, 3/8"	<b>6.2</b>	283	<b>6.2</b>	300
Gamblin Refined LO, 1/8" 90F	<b>6.4</b>	17	<b>6.2</b>	270
Gamblin Refined LO, 1/4" 90F	<b>4.7</b>	17	<b>4.8</b>	270
Gamblin Refined LO, 3/8" 90F	<b>5.3</b>	24	<b>5.6</b>	270
Gamblin Cold Pressed LO, 1/8" 90F	<b>6.4</b>	30	<b>6.7</b>	270
Gamblin Cold Pressed LO, 1/4" 90F	<b>5.0</b>	27	<b>5.4</b>	270
Gamblin Cold Pressed LO, 3/8" 90F	<b>4.9</b>	33	<b>5.3</b>	270
Boiled Linseed Oil	<b>2.5</b>	9	<b>3.4</b>	1450
Boiled Linseed Oil w/ drier	<b>-1.8</b>	6	<b>1.1 *</b>	1450
Cadmium Orange, pan test	<b>-0.5</b>	14	<b>2.4</b>	1450
Burnt Sienna, pan test	<b>1.7</b>	9	<b>4.4</b>	1450
Cadmium Orange, 200 μ on canvas	<b>~ 7</b>	16	<b>0</b>	3-4 yr avg
Cadmium Orange, 70 μ on canvas	<b>~ 6</b>	11	<b>-7</b>	3-4 yr avg

\* Change after initial solvent evaporation

### Swab Tests of Paintings

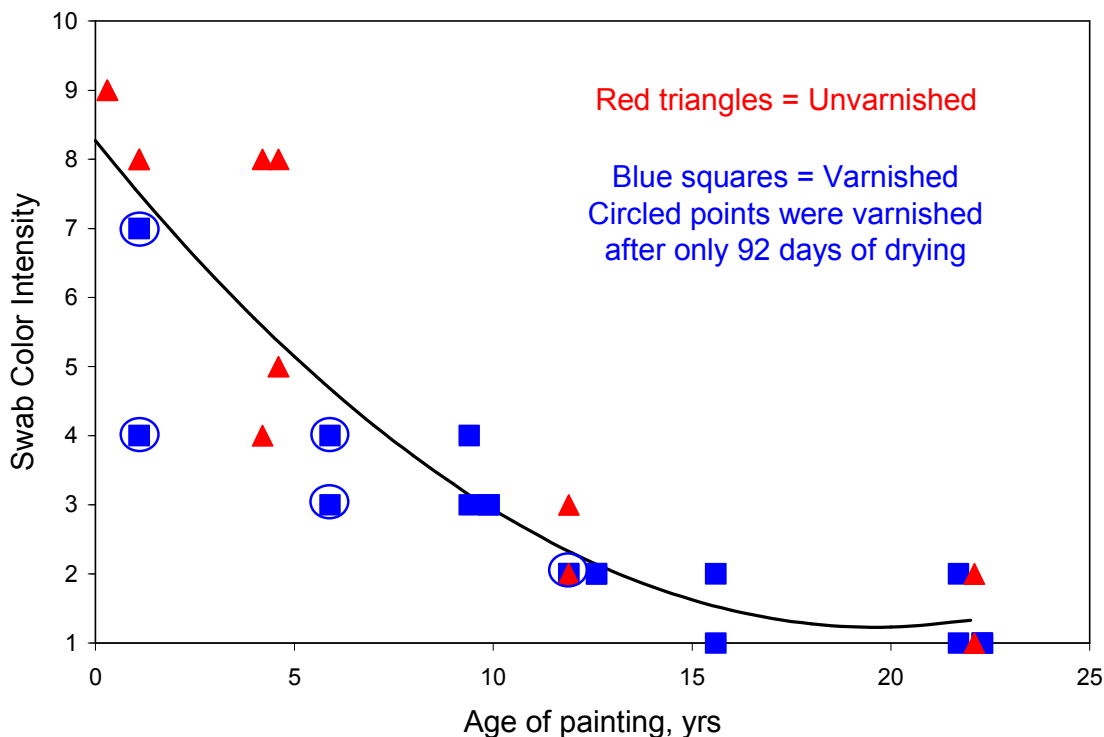
A swab test is a method aimed at estimating the relative ease of paint removal from a painting. It consists of firmly scrubbing a small spot on the painting with a turpentine-soaked cotton swab and visually assessing the amount of coloring picked up by the swab. The method is further described at the end of Appendix A, if you would like to try it out.

## Effect of Painting Age

The swab test was applied to paintings with a wide range of ages. Fortunately for this investigation, being in love with my paintings despite being counseled that none of them are precious, I have saved a lot of paintings and have their history recorded. From this inventory, a range of ages from new to over 20 years old were available for the swab. Furthermore, the paintings selected had both an orange and a green area to test.































The results are most interesting! The amount of paint removed depended on the age of the painting, as indicated in the photo of the swabs on the next page. In fact there is a trend with age, less paint being removed from older paintings. Only paintings over about 12 years old possessed rock-hard paint layers and showed only very slight or no paint removal in the swab test.

By converting the swab photo to black and white, a value-scale number could be assigned to the color intensity of each swab (10 black – 1 white). Granted this is an estimate, but the results show a reasonable trend, as shown in the figure below:



Most significantly, these results are entirely consistent with, and explained by, the transformation of the linseed oil in the paint from an organic polymer to an ionic-compound-containing polymer, as found by van den Berg. As the aging linseed oil becomes more “ionic,” the paint’s susceptibility to removal by a turpentine scrub will decrease, which is exactly what we see here. Think of it as

the paint becoming less soluble with age, although it's not really *dissolving* in the swab test but is being abraded.

Age of painting in years	Days painting was dried before varnishing	Cotton Swab Test	
		On Orange Paint	On Green Paint
0.3	Not varnished		
1.1	Not varnished		
1.1	92		
4.2	Not varnished		
4.6	Not varnished		
5.9	92		
9.4	304		
9.9	215		
11.9	92		
11.9	Not varnished		
12.6	182		
15.6	273		
21.7	243		
22.1	Not varnished		
22.3	515		

Results of applying the cotton swab test to paintings of different ages. As paintings get older, less and less paint is able to be removed. Similar removal is seen from orange and green painted areas.

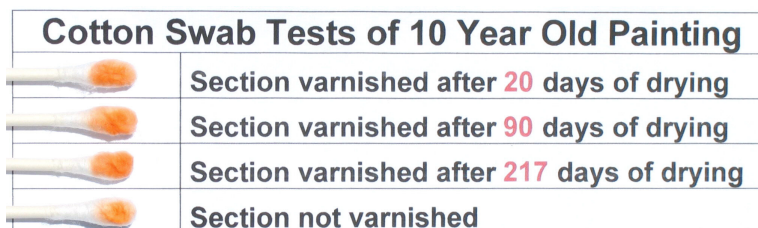
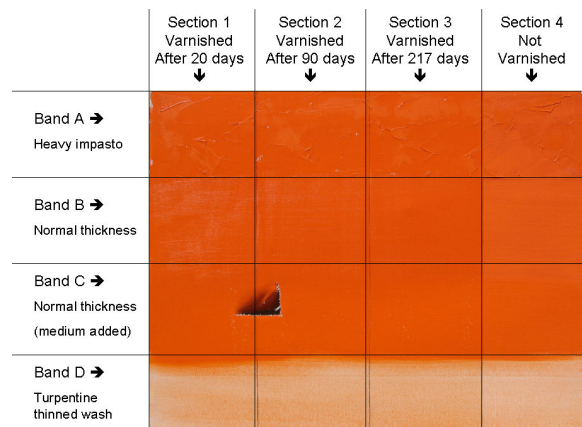
Some of the paintings tested were varnished, others not. Some were varnished after only 92 days of drying. Based on the figure, the varnish history had no discernable effect on the overall trend with age. The amount of paint removed – the strength of the paint film, the conversion to the ionic form – was simply not affected by varnishing!

To summarize, these swab results show that (1) oil paintings take a long time - over 12 years - to become fully aged to a very hard film, and (2) the presence of a varnish does not retard, or accelerate, this aging process. The varnishing simply doesn't matter.

## Effect of Drying Time Before Varnishing

The most important experiment performed was a direct test of varnishing after different curing times. The experiment started in 1998 by painting a 16 x 20 stretched canvas with cadmium orange – the color of the sun according to the late master artist Charles Sovek. The painting was divided into four horizontal bands representing different painting methods: (A) a heavy impasto band, (B) a band of normal thickness, (C) another normal band using a medium (stand oil in turpentine) added to the paint, and (D) a band of a turpentine-diluted wash. As the painting dried, varnish (Liquitex Soluvar) was applied but only in vertical sections, across all of the bands. The first section was varnished after 20 days of drying, the next section after 90 days, and the last section after 217 days. The final section was left unvarnished.

The painting then sat in the studio and in a closet (where it got the tear) for over ten years, whereupon the swab test was applied to the sixteen individual sections to see what has happened. At the time, it was suspected that the paint layer would be harmed by varnishing too early. This could result in more paint being removed for those sections with the early varnishing. Surprisingly, the amount of paint removed was essentially the same across each band! In other words, neither the presence of varnish nor the drying time before varnishing had any effect on the status of the underlying paint layer. This was observed for all the bands, A, B, C, and D. This photo shows the swabs from band B:



After five more years of storage, the painting was tested again. The swabs for each band are shown in the photos on the next page. Swabs from Bands A, B, and C are similar in color intensity. Most importantly, there appears to be no difference between the three varnished sections within each band, the same paint removal occurs after varnishing on day 20 as opposed to day 90 or day 217 (which is beyond the six month manufacturer's recommendation). The swabs from the varnished sections have a larger zone of color than the unvarnished ones. This is believed to be caused by the presence of the varnish that is dissolved by the scrubbing. This dissolved varnish may help spread the removed paint to all parts of the exposed side of the swab. In contrast, the swabbing of the unvarnished sections felt much "drier" during the scrub.

## Swab Tests of Fifteen Year Old Orange Test Painting

Swabs are in the following order:

1. Varnished after drying for 20 days
2. Varnished after drying for 90 days
3. Varnished after drying for 217 days
4. Unvarnished

1

2

3

4

### Band A

Thick impasto



### Band B

Normal thickness



### Band C

Normal thickness  
with stand oil/  
turpentine  
medium



### Band D

Thin wash



The paint removed from Band D is less than the others because there is only a thin wash present. However, the thin wash enables visual observation of the paint removed from the painting itself – white spots appear equally where the band D sections were swabbed, further evidence that varnishing just doesn't matter.

There is no doubt that much more paint is being removed from this Orange Test Canvas than should be for a fifteen year old painting, based on the swab results with the paintings of various ages. This can be rationalized by proposing that prolonged storage in the dark, as occurred in this case, has slowed the normal aging process. In particular, the transformation of the polymerized linseed oil from organic to ionic seems to have been retarded in some way. This unexpected development is unfortunate but does not diminish drawing the important conclusion that the drying time before varnishing had no effect on the underlying painting.

## Chapter 4 Conclusions

To try to answer the question of when to varnish, we need to merge the findings from the experimental work from Chapter 3 with the knowledge base that exists for linseed oil based paint and varnishes from Chapter 2. It's time to draw some conclusions! So, here goes a healthy mix of facts and theory:

- Linseed oil, by itself and in paint, undergoes an initial reaction with oxygen that leads to the conversion of the viscous liquid to a flexible solid.

For paint spread out as a layer, this initial reaction takes place during the first 1-3 weeks, depending on factors like paint thickness, presence of driers, temperature, to name a few. It is not important to pin down a specific, universal time; each painting can be different. It will be obvious when the surface is firm and dry to the touch.

- Once the solidification starts, further reaction with oxygen becomes very slow.

The polymer does not allow oxygen to diffuse in nearly as fast as the starting liquid. Oxidation, and the accompanying cross-linking, is mostly over.

- Further reaction with oxygen, after the initial solidification, does not contribute significantly to the paint film becoming stronger.

It is already polymerized. The amount of additional oxygen incorporated is small. Fragmentation to volatile products begins, which hinders the prospects for further beneficial cross-linking. The linseed oil structure is breaking down long term; the opportunity for cross-linking is diminishing.

- If oxygen is indeed not that necessary, or even desired, long term, then the possibility of a varnish layer limiting oxygen availability is moot.

The organic-to-ionic transformation requires water. Any role of oxygen in this long-term aging process would be most unexpected. The fragmentation reactions *could* involve more oxygen. But, neither of these aging reactions (ester hydrolysis, oxidative fragmentation) is desirable, so why worry about long-term oxygen transport?

- Even *if* extra oxygen would be beneficial long term, the presence of a varnish layer will not appreciably hinder oxygen diffusion over the restriction already imposed by the paint.

A varnish layer is, by nature, a much thinner layer than a normal paint layer. Thinner helps with oxygen diffusion. As an organic polymer, varnishes are just as permeable towards oxygen, if not more so, than

cured linseed oil. Diffusion will always be limited by the paint more than the varnish, in part because of the presence of solid, non-porous pigment particles. There is also the diffusion path from the back side of the painting (except for paintings on metal). Probably not great, but nothing is at this point!

- It is unlikely that the underlying paint will undergo sufficient expansion or contraction to cause the varnish to crack.

Using modern, professional grade artist's paint, appreciable expansion and contraction are very improbable within the first year - when the varnishing will occur. If the varnish eventually cracks for this or another reason, then remove it and re-varnish. The risk of this happening is judged to be very remote.

- Most importantly, there is nothing magical or special about 6-12 months of drying.

There are really only two time frames that matter: the first few weeks (curing), and a very long time (aging). Nothing is gained by waiting 6-12 months. The main oxidation is over and the long term changes are barely starting.

So, how long should a painting dry before it's varnished? My answer: three weeks, since that was demonstrated in this study; maybe even sooner. All that is required is that the entire paint surface be dry enough for the varnish to be brushed on without dissolving any paint. Other than that, I see no advantage for waiting for any longer. The paint will eventually harden and age independent of varnish. There's certainly nothing wrong with waiting six to twelve months, especially if you're not in a hurry, but I say no more prison sentences!



## Biography

A native of Texas, Chuck Mauldin has been painting in oil and drawing in pastel and charcoal since the age of twelve. His interest in watercolor and pencil drawing grew during his years spent in Louisiana. The artist uses this variety of media to portray a broad range of subject matter, in a realistic yet painterly style. Striving to quickly capture color and mood with a direct "alla prima" technique is one of his main objectives in painting outdoors on-location (known as "plein air" painting). Workshops with Charles Sovek, George Strickland, Ted Goerschner, Jan Kunz, Tony Van Hasselt, Jeanne Dobie, and Tom Lynch have played a significant role in his development as an artist. Chuck has won numerous awards in exhibitions around southern Louisiana and has had work accepted into regional and national juried competitions. He is a member of Oil Painters of America and has achieved Signature membership status in the Louisiana Watercolor Society and the Plein Air Artists of Colorado.

After 28 years in Louisiana, Chuck and his wife, Barbara, moved to Fredericksburg, Texas, in March of 2005, in order to pursue their passion for art on a full-time basis. Chuck's website, [www.chuckmauldin.com](http://www.chuckmauldin.com), went on-line in October of 2005. His work is displayed at the following galleries: Fredericksburg Art Gallery, Fredericksburg, TX; Lee-Bunch Studio Gallery, Del Rio, TX; Martin's Frame Factory and Gallery, Baton Rouge, LA, Brookwood Gallery, Brookshire, TX.

Degrees in chemistry from Southern Methodist University (B.S.) and the University of Texas (PhD) led to Chuck's career in research at ExxonMobil Process Research Labs in Baton Rouge, Louisiana. He presently holds 56 U.S. patents in the field of catalysis. Most of these dealt with titania supported cobalt catalysts for the conversion of hydrogen and carbon monoxide gas to liquid hydrocarbons (known as the Fischer-Tropsch synthesis). A catalyst that Chuck invented was the centerpiece of a 20 year research effort aimed at using large natural gas reserves in geographically remote areas to make premium diesel and jet fuels and lube basestocks.

# Appendix A Summary of Experiments

One of the methods used to measure weight changes utilized 2.5 inch diameter aluminum pans. For most tests, small metal Woodruff keys of known thickness were placed in the pan and used as a marker to estimate the depth of the oil. The pans were allowed to stand, with a glass cover suspended above to protect from dust but positioned to allow normal air circulation and exposure to normal room light. Two weigh scales were used, calibrated with a standard metal weight. These inexpensive scales only measured to hundredths of a gram, so tests of very thin films were not feasible.

## Weight Changes of Linseed Oil

Figure A-1 shows the changes in weight for three tests of a sample of Gamblin refined linseed oil. The three tests differed in the depth of oil present, which affected the rate of weight gain and the final amount gained. The smaller the depth, the faster the rate and higher the final gain. There is a volatile solvent present as indicated by the early weight loss. After the induction period where weight is constant, the oxidation-generated weight gain begins. Weight stabilizes again after gains of 6-8%, when the surface forms an oxygen-resistant skin. This pattern is seen again with Gamblin cold pressed linseed oil, as illustrated in Figure A-2. There was no solvent evaporation, but the induction period with this oil was extremely long.

Figure A-1  
Pan Tests of Gamblin Refined Linseed Oil

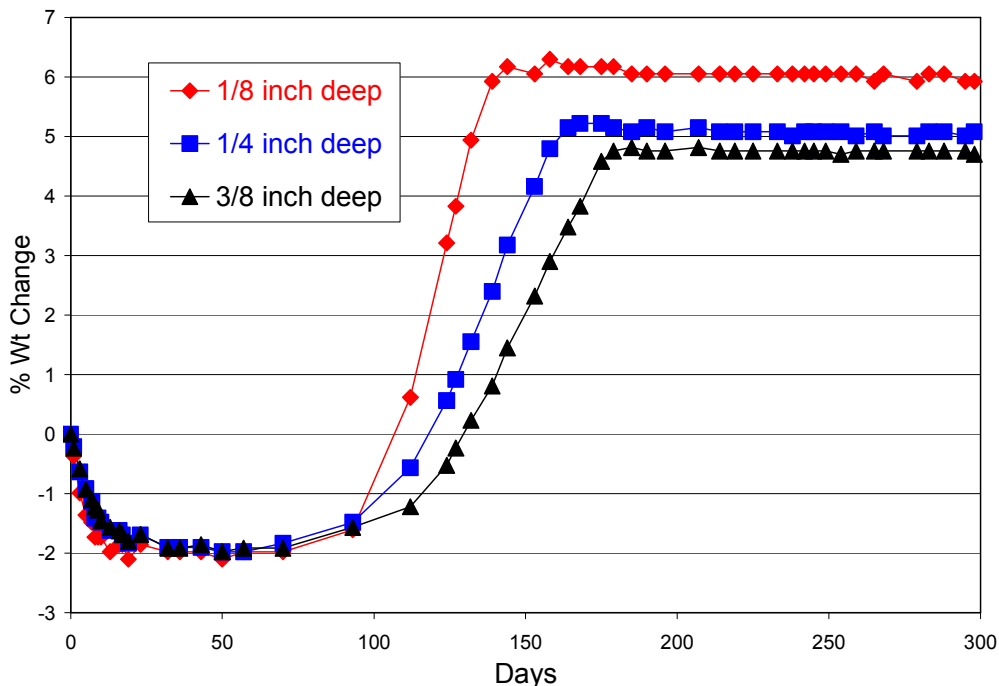
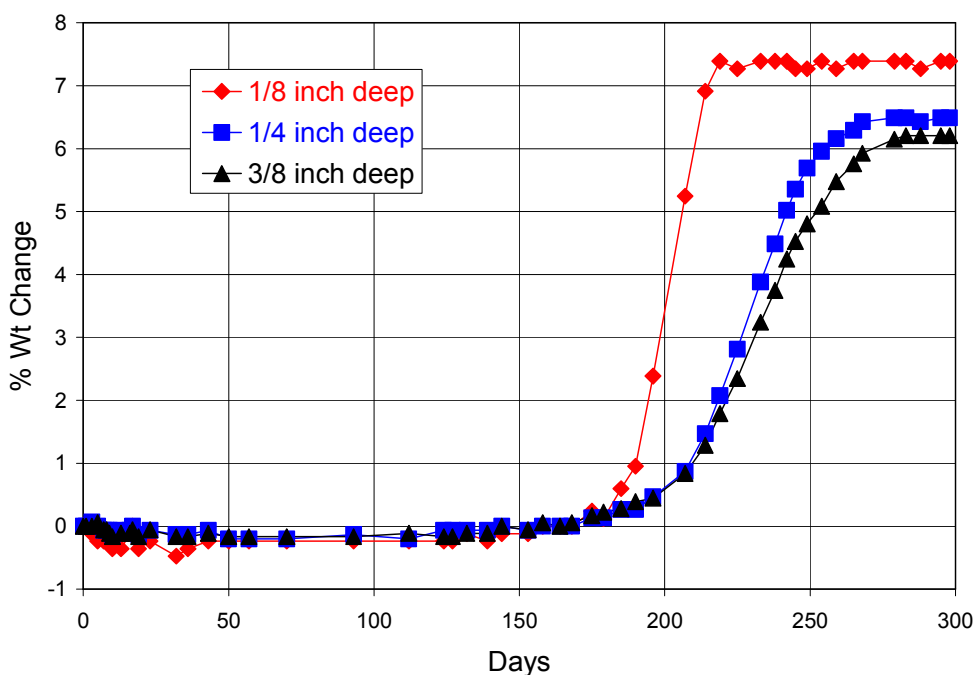


Figure A-2  
Pan Tests of Gamblin Cold Pressed Linseed Oil



The two Gamblin linseed oils were also tested at 90 F, using an open kiln heated with an infrared lamp. Results are shown in Figures A-3 and A-4. Higher temperature has a pronounced effect, as expected. The induction period is greatly shortened for both oils, with the cold pressed still the more sluggish to start reacting. The higher temperature increases the rate of weight gain, as it should. However, the final level of weight gain, roughly about 6%, is similar to the room temperature results. After the initial 90 F conditions, the pans were allowed to stand at room temperature. As shown on the right side of the figure, weights show no change out to 225 days. Again, things “stop” when the oil surface solidifies.

A sample of boiled linseed oil, sold by Houston Art & Frame and obtained many years ago, was tested as-received and after addition of Grumbacher Japan Drier (an oil soluble cobalt-based drying promoter). Results are shown in Figure A-5. The base oil underwent an immediate weight gain that lined out at about 2.5%. The lack of an induction period is believed to result from the oil already being significantly oxidized by the “boiling” processing. The 2.5% gain, compared to the 6% seen with the Gamblin oils, is also consistent with this oil being “pre-oxidized.” The addition of the drier caused an initial drop in weight, explained by the evaporation of a solvent in the drier. By adjusting the weights to the weight at day 19 instead of day 1, i.e. after the solvent evaporation, essentially the same weight gains are found for the boiled oil independent of added drier. This is illustrated in the bottom chart of Figure A-5. Later, it was learned that boiled oil likely already has a metal soap drier present, so the added drier is redundant. This chart is particularly important because it shows that a slow, small gain in weight continues to accumulate after day 19. From this point, a gain of 1% has occurred after 1400 days (about 4 years).

Figure A-3  
Pan Tests of Gamblin Refined Linseed Oil, Started at 90 F

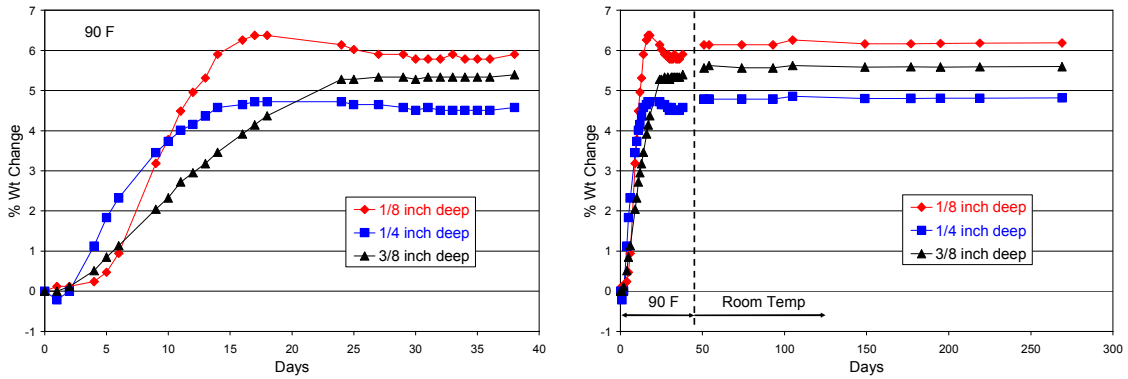


Figure A-4  
Pan Tests of Gamblin Cold Pressed Linseed Oil, Started at 90 F

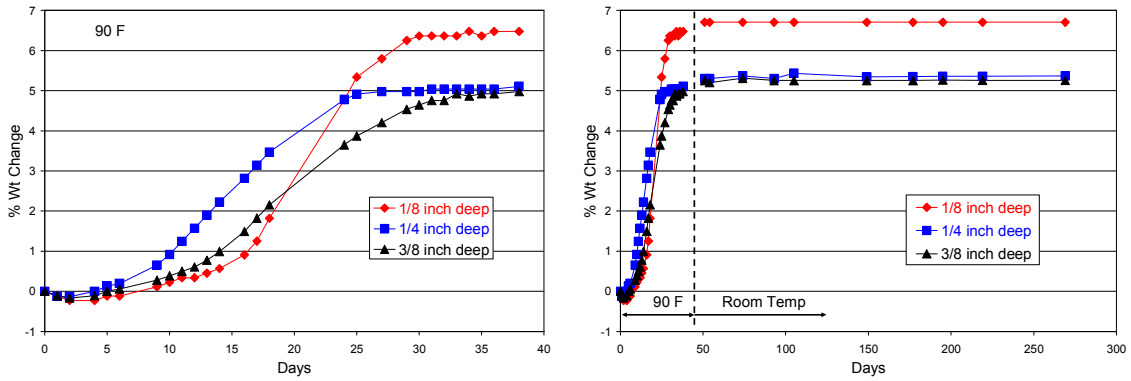
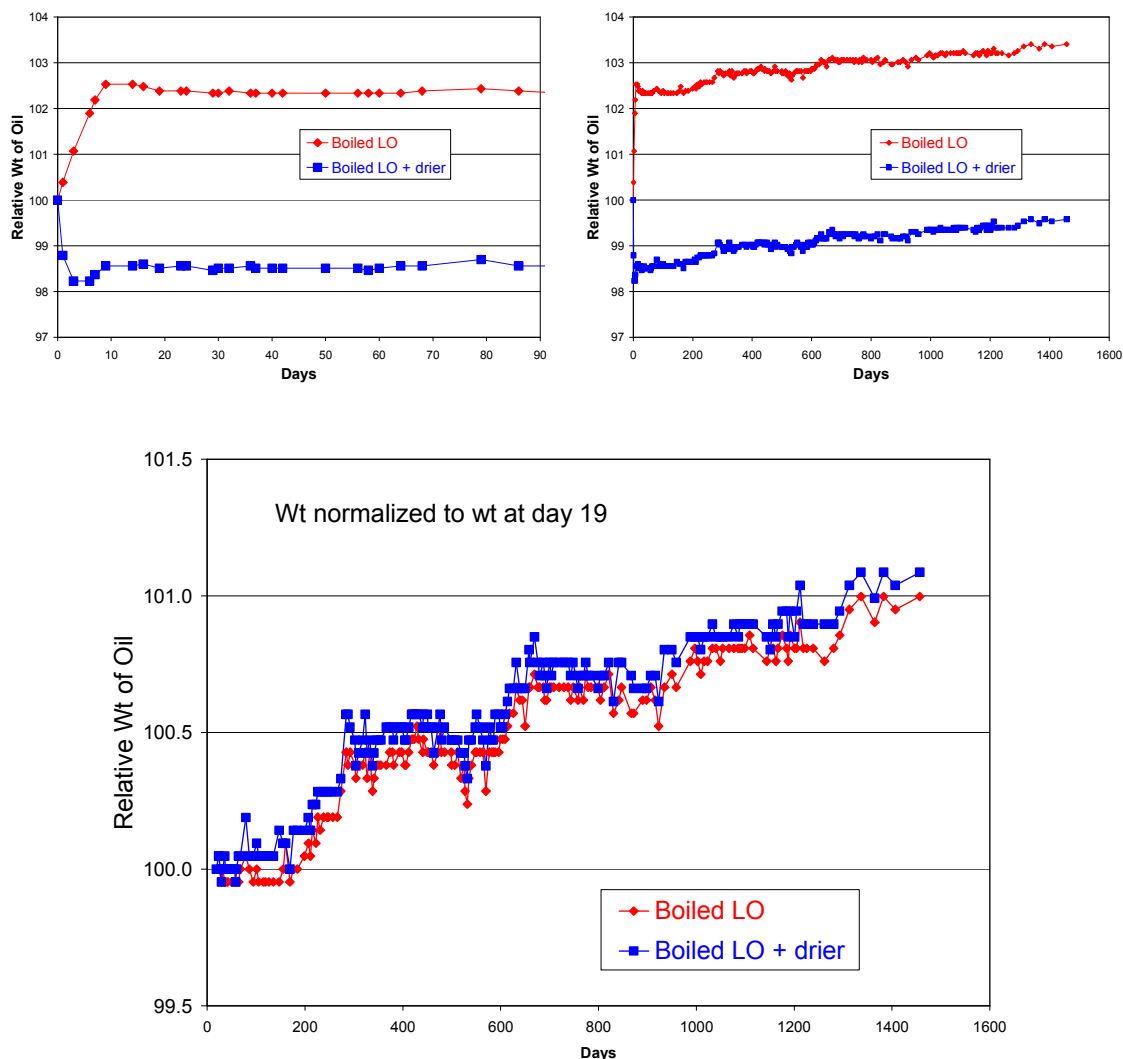


Figure A-5  
Pan Tests of Houston Art Boiled Linseed Oil



### Weight Changes of Paints

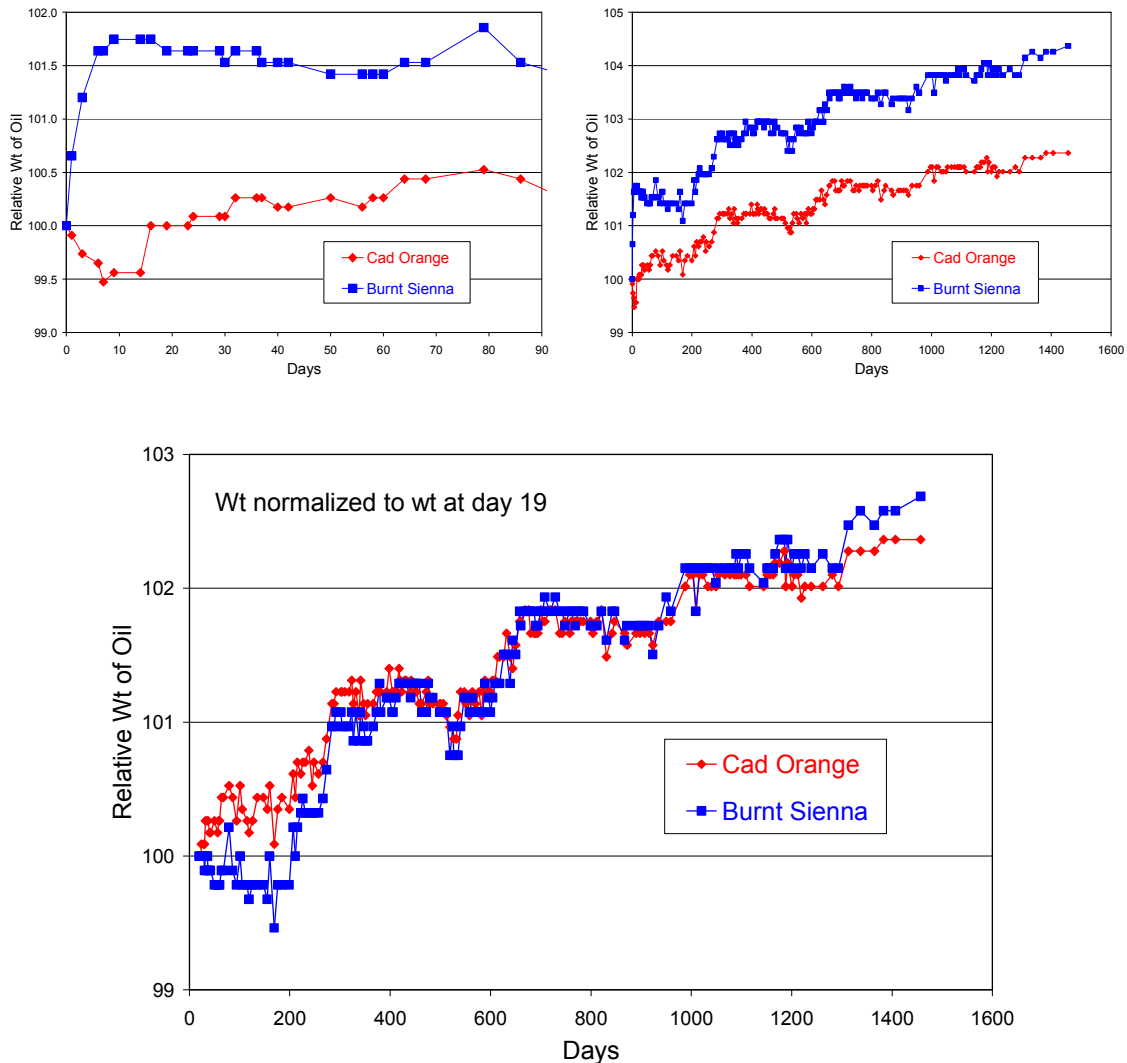
Pan tests were made using Cadmium Orange (Utrecht, PO20 in alkali refined linseed oil and expeller pressed safflower oil) and Burnt Sienna (Utrecht, PR101 in alkali refined linseed oil). Depth of the paint in the 2.5 inch diameter aluminum pans was about 3/8 inch. The pans were kept at room temperature while weight was measured over time. Results are shown in Figure A-6, expressed as the change in oil weight (calculated using a starting oil concentration of 23% for Cadmium Orange and 25% for Burnt Sienna).

The Burnt Sienna showed a rapid, initial weight gain of over 1.5%. The Cadmium Orange lost weight initially, so something volatile was present in this paint. As shown in the bottom portion of Figure A-6, weight was gained at very similar rates for both paints after day 19. Over the four year test, the weights

showed periods of gain, then periods of no gain or small loss. The pattern is an annual one, with the gains occurring during the summer and the no-gains occurring during the winter. Changes in humidity, more than changes in room temperature, are felt to be the root cause of this “wiggle” to the overall pattern of gain.

These paint samples did not change in appearance. No apparent shrinking or cracking occurred out to 1400 days (4 years).

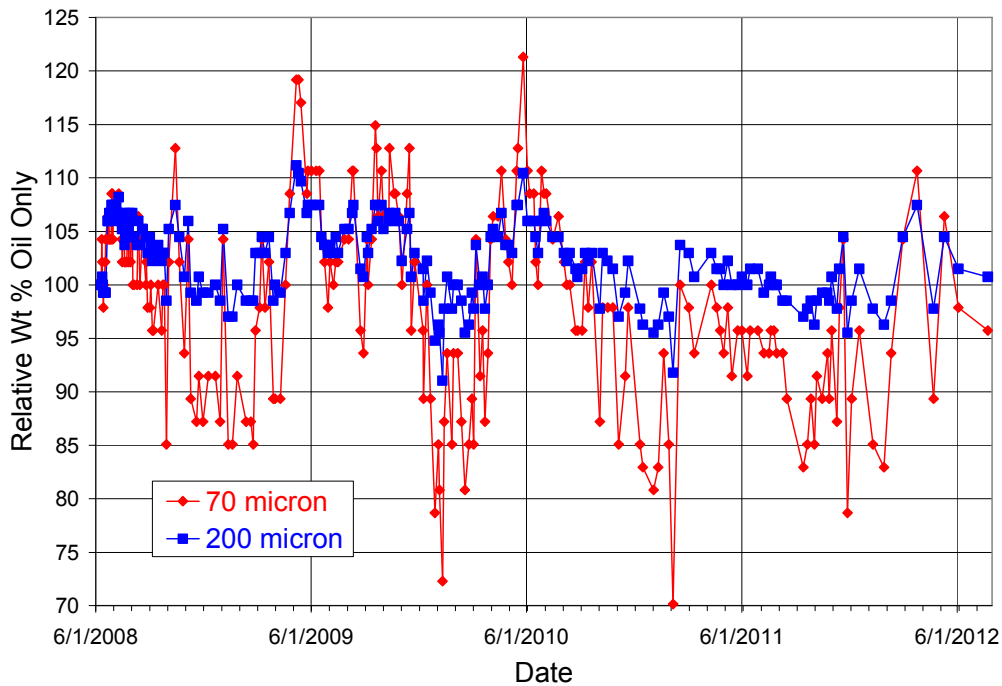
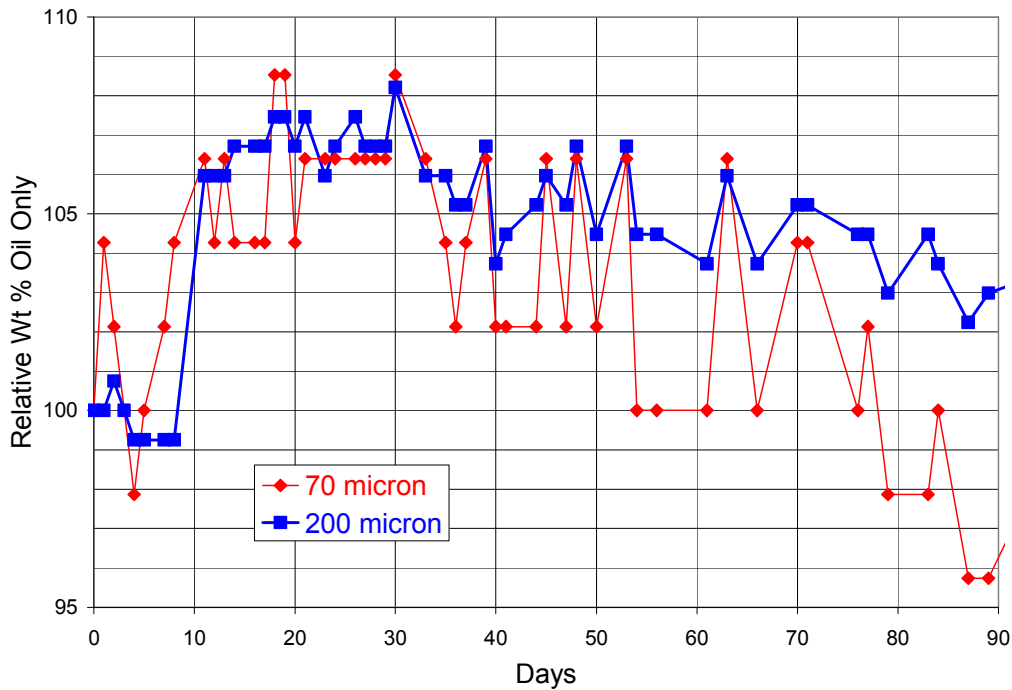
Figure A-6  
Pan Tests of Cadmium Orange and Burnt Sienna Paint



An attempt was made to measure weight changes on “actual paintings.” For these tests, 2 inch diameter, 4 inch high, cylinders of 12 oz acrylic primed canvas were painted with Utrecht Cadmium Orange. One cylinder was painted with a “normal” thickness of paint. A second cylinder was painted with a much thicker layer. Using the surface area painted and a measured paint density of

2.13 g/cc, the average depths of the paint on the two cylinders were estimated to be 70 and 200 microns. The painted canvas cylinders were kept at room temperature while the weights were measured with time. Results are shown in Figure A-7, again expressed as the relative weight of only the oil portion of the paint.

Figure A-7  
Canvases Painted With Cadmium Orange



The upper part of Figure A-7 shows the oil weight changes over the first 90 days. Both thicknesses of paint gain about 7% by day 20, which is very consistent with the initial gains seen in the linseed oil tests. After that, the 70 micron paint layer loses all that weight and more! The 200 micron paint layer loses some weight as well. In the chart in the lower part of Figure A-7, the results over the four year test continue this pattern of gain followed by loss. So, what is going on here? I do not believe these weight changes are actually occurring with the oil. The problem is that we are trying to measure very small changes of a relatively small amount of paint. The wider variation (“scatter”) seen in the data for the thinner paint film bears this out. The ups and downs follow an annual pattern. Hence, the weight changes are most likely caused by seasonal changes in humidity and room temperature, masking any changes of the oil. The cotton canvas part of the measured weight will be especially sensitive to humidity changes. So, unfortunately, these tests with “real paintings” have failed to provide clear indications of how real paintings change over the long term. However, the initial weight gains are likely valid because the effects of ambient conditions are not as great over a short time frame.

### **Swab Test Procedure**

Dip a swab in clean turpentine and lay it on the painting. Slowly and firmly rub the swab in a small circular motion for ten revolutions (counterclockwise in the northern hemisphere – just kidding!!!). Don’t twirl the swab; leave the same side facing the painting. Lift and observe. The exact method is not as important as trying to do the method the same way every time. Be careful in trying this on thinly glazed areas, where the amount of paint removed could be noticeable. You will need to re-varnish the test area or you’ll have a dull spot. Note that the firm, rubbing motion is important. Other varnish removal methods tried, such as blotting with small pads and soaking small cut-out pieces in turpentine, did not remove any paint.