The Actual Secrets of the Old Masters, part I

Hand Refined Linseed Oil – Tad Spurgeon

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There have been many theories over the centuries about the "secrets of the Old Masters." But all claims to have found the magical potion have subsequently been disproved, and modern technical art history has shown through decades of research that the materials of older painting are straightforward on the surface. However, if we look underneath the surface, we find that many materials have morphed over the centuries to the point that they no longer resemble their historical relatives. Such is the case with the complex material called, almost always too casually, linseed oil.

The 20th century produced a simplified painting system based on various combinations of damar varnish, turpentine, and stand oil. But the research by the National Gallery in their yearly Technical Bulletins published since 1980 shows that, prior to the 19th century, there is no such thing as global use of resin the paint film. In fact, resin in older painting is principally limited to "small amounts of pine resin", and use is quite sporadic, primarily as a way to get a specific pigment to dry more quickly.

A detailed investigation of this subject would require a book of its own. However, the NGTB research analysis does suggest three distinct general patterns of medium use in older painting. These can be described broadly as early, middle, and late, but it is more accurate to call them egg-oil, oil dominant, and resin-oil. The earliest pattern involves a combination of oil and egg as the medium for the paint, and is coming to be more widely known for earlier painting. It also now appears that, as late as the 16th century, Lotto made a complex *tempera grassa* medium. The oil dominant pattern begins in the 15th century and features many paintings made with oil alone, some with heat-bodied oil, and some with an addition of "a little pine resin" or egg as well. The use of resin or egg in the this approach is not global, but is reserved for a specific colour or passage. A small amount of added resin such as silver fir or larch balsam gives the oil slightly more set and drag, making edges cleaner, and could be used without additional solvent. But the pattern of resin use is complex. Early Flemish painting often uses resin to help a red lake glaze to dry (NGTB 18). Yet, in the samples analyzed from *The Arnolfini Portrait* (1434), the green uses resin (and the pigment is not "copper resinate," copper acetate ground in resin to seal it) while the red lake does not. The use of heat-bodied oil also suggests the possible use of litharge or white lead as a drier, but the presence or absence of these cannot be detected. The oil based system continues through the 17th and 18th centuries: both Jan Steen and Canaletto use heat-bodied linseed oil and no resin (NGTB 19). Research "suspects" – stated in *Rubens Unveiled*, (2012) by Nico Van Hout and Arnout Balis – that the rheology of Ruben's paint was influenced by an addition of egg white. A noticeable change is Rembrandt's use of chalk, and ground calcite as a medium ingredient for Velásquez. It is worth noting that these painters, in their search for ingredients to increase an element of thixotropic grab globally in the system, chose ingredients other than resins. While this approach may seem too simple on the surface, the following section illustrates that the oil can be modified to many different behaviors, that "a small amount of pine resin" can also be implemented in a variety of ways, and that the addition of calcium carbonate to the system creates an entirely new dimension.

The resin-oil medium pattern is more varied in terms of materials, and more individualized from painter to painter. It also features the global use of resin in the paint in certain cases, and more in the way of "lost secrets" medium experimentation that led to technical issues. The oil-dominant pattern does extend through 19th century usage, however. Analysis of Impressionist paintings suggests very little use of even simple resin preparations, Constable's *The Hay Wain* (1821) was painted with heat-bodied linseed oil and used heat-bodied walnut oil for the white (NGTB 19). On the other hand, this is also the era of the notorious mastic gel, lead acetate, and various experiments involving copaiba balsam and gum elemi, and Constable's late work has been shown to contain the traditional sequestering trio of beeswax, resin, and egg. Later in the century, amber varnish has a brief heyday in England, and, apparently starting in Germany, use of damar begins. While

much of what was done in the 19th century worked, the fallout from more complex "nostrums" that did not led to the simplified 20th century approach to the medium.

The Oil

The traditional oils for painting were long thought to be linseed oil in the colder north and Spain, and walnut oil in Italy, but recent research has revealed a more general use of both than was previously known. This is aligned with research which suggests a highly developed trade network for painting materials throughout Europe even by the 14th century. Poppy oil began to be used in Holland in the 17th century and is associated with floral specialists. Linseed oil can dry the fastest, but also has the most potential to yellow: the De Mayerne Manuscript has many recipes designed to improve linseed oil, the painter's opinions recorded there are generally in favor of walnut oil, although Van Dyck prefers linseed oil. Poppy oil is slow drying, the least yellowing of the traditional oils, but can wrinkle if too much is used in a layer. Walnut oil can provide a happy medium, especially if used in a climate that is warm and dry, but walnut oil does not lend itself naturally to more bravura or broken-surface paint application the way linseed oil does. This can, however, be changed by using a denser medium. Both safflower oil and sunflower oil – refined, nearly colourless – can also be used for painting. While they are non-yellowing, they are also very slow drying. Small additions of these can be used for colours that otherwise dry quickly in the tube, or in an oil medium to extend the open time, allowing for a single alla prima layer to continue over many days. Commercial safflower or walnut oils which dry surprisingly quickly do so because they have added driers.

The debate about the best oil to use for painting has gone on for centuries. This makes sense when one realizes the extent to which older painters knew and trusted the specific type of oil with which they worked, this obviously became "the best." Much is sometimes made of the film strength of linseed oil versus walnut oil, but most Italian Renaissance paintings were made with walnut oil, and are still with us. Much is also made of the potential of linseed oil to yellow, based on the experience in the 20th century with hot-pressed oils coupled with the generally debilitated craft of the period. While the availability of cold-pressed, highly refined linseed oil has solved the overt darkening issue, this oil is so refined that it does not tend to dry well, a period of four or five days is common in tests. However, an organic cold-pressed oil, hand refined using the method below, will dry in one or two days and only yellow to the extent of walnut oil, less if aged in the traditional manner in the light. It is important to look not only at the type of oil, but at its original quality, and how it has been subsequently processed: printed remarks about "the oil" seldom take any of this into account, and can therefore be misleading. Walnut oil is naturally better suited to finer or thinner painting, linseed oil to working with more force, but each can be modified somewhat towards the other quality. All this being said, the best oil for a given painter may well be the one of highest and most predictable quality which is readily and reliably available.

Paint Film Basics

Plant oils are very complex chemically: dense tomes are written about edible oil chemistry, and there is no such thing as a generic "oil" molecule. Rather, oil is made up of quite large molecules called triglycerides which have various, also large, water soluble fatty acids loosely attached to them. Fatty acids are better known now as Omega-3, Omega-6, etcetera, for their positive role in human nutrition. The variety of the fatty acid make-up is what makes one oil dry differently from another. The proportion of linolenic (Omega 3) and linoleic (Omega 6) acids in walnut and linseed oil, for example, is different, linseed having significantly more linolenic acid than walnut. Linolenic acid is the most chemically reactive of the group, making linseed oil the faster drier, but also the oil most

likely to yellow over time due to byproducts of the polymerization process. Only the triglycerides polymerize, or "dry," the fatty acids do not. Refining the oil removes a miscellany of impurities and reduces the fatty acid content significantly, making the same thickness of paint film that much stronger and less likely to yellow. Polymerization is a complex reaction with atmospheric oxygen which takes place over very long periods of time; even linseed oil which has been dry for months and is safe to paint over will still be polymerizing for years to come. Oxygen, in conjunction with heat and sunlight, has the potential to eventually desiccate the oil altogether. If the paint film is thin, or underbound through the use of solvent, this can begin to happen in a matter of decades. If the paint film is thick, uses preheated oil, or is protected by a varnish layer, this process can be slowed for many centuries. However, thicker oil can have more of a tendency to yellow, and is best used with moderation no matter how good the oil is. Creating a working balance here is a matter of knowing the behavior of one's materials relatively well. This happens naturally in practice as nothing is more important than knowing at what point, or under what conditions, a thick or viscous final layer of paint may darken on drying.

Raw oil alone is quite thin, and, especially when used with solvent as a medium, may not make a strong enough paint film to adequately withstand the attack of oxygen over time. Oil paint thinned with solvent in the manner of watercolour thinned with water does not tend to hold up well. This is especially true if the painting is never varnished. The premature aging of many 20th century paintings made with the somewhat misguided conceptual purity of paint alone attests to this. The hot-pressed, alkali-refined oil of mid-20th century American commercial paint is relatively volatile with regard to its drying characteristics, and the most likely to darken; so-called "artist's" linseed oil from this period can be so hopeless that it forms a dark brown, soft gum instead of hardening. When reading the comments of writers on what they term linseed oil, it is important to take the time period into account. Also, the words "linseed oil" in these cases typically refer to the readily available commercial oil of the period. For most of the 20th century, this was not even a cold-pressed oil. One of Laurie's early texts mentions refining the oil and gives a method, after this no 20th century text in English goes into refining the oil at all.

Commercial paint always uses new, raw oil. While the paint appears to be "rich" and, of course, "buttery," these qualities are from additives. Given the nature of commercial paint, a medium is virtually necessary to enhance the longevity and character of the paint, as well as to keep the paint from drying down in layers, the dreaded "sinking in."

When a resin is added to a paint film, much more complexity occurs in the aging process. This is especially true of a spirit-resin type medium such as damar, a balsam, or mastic. The use of resin in oil paint is arguably ancient, going back to its origin as a decorative outdoor paint. Paint made with boiled oil and a hard resin varnish such as copal or sandarac would last much longer outdoors. However, the necessity for the paint to maintain its true colour over time was not as dire. Warnings about the overuse of resin causing brittleness and ultimate darkening in the paint film have been coming from scholars and conservators for many decades. It is important to always formulate a paint film with the absolute minimum amount of resin if using resin should prove helpful or unavoidable. Research into paint films that are centuries old (NGTB) indicates that small amounts of resin can be used safely. This is logical because the behavior of the stronger oil component then remains dominant during the aging of the paint film.

The traditional alternative to using resins is a paint film which relies on a somewhat thicker, preheated oil and possibly a mineral addition as well, such as chalk, calcite, or silica, all of which have been found in older paintings. The thicker vehicle allows the pigment particles to float, and helps keep the action of oxygen at bay by sealing the surface of the painting more effectively. The stone dusts allow the exploration of many different types of paint

rheology and viscosity, and, in the case of the calcium carbonates, create a stronger paint film over time. That this system works well over time is demonstrated by the condition of most Rembrandt paintings, noted consistently by scholars and conservators as unusually good in spite of what they have often been through in over four centuries.
Chemically, the yellowing of linseed oil occurs as a by-product of the polymerization process. Conjugated unsaturated hydroperoxides are converted into conjugated unsaturated ketones, which can then produce long-chain polyenes with a yellow colour. If the hydroperoxides are reduced, or eliminated, this process can be curtailed before it begins. "Semi heat-bodied oil" is often found in older paintings in the NGTB research. A study done titled *Long-Term Behavior of Oil-Based Varnishes and Paints, Fate of Hydroperoxides in Drying Oils* by Jacky Mallgol, Jean-Luc Gardette, and Jaques Lemaire of the Laboratoire de Photochimie Molculaire et Macromoléculaire at Universite Blaise Pascal (JAOCS, vol. 77, no. 3 (2000)) shows the way in which a specific amount of heat (from 25°C to 120°C) applied to linseed oil first generates, then eliminates, the hydroperoxide population of the oil. The amount of hydroperoxides generated, and the amount of time to both create them and eliminate them, decreases with greater amounts of heat. According to the study, (done with a commercially refined linseed oil provided by Pebeo), at 25°C hydroperoxides peak at 600 hours, then have declined markedly by 1200 hours. This amounts to three months storage at slightly above average room temperature, and might well be approximated by a temperate zone summer in a south facing windowsill. At 120°C hydroperoxides peak at one hour, and are eliminated at ten hours. Extrapolation based on the other temperatures involved suggests that at 150°C hydroperoxides would peak at half an hour, then by eliminated after four hours. This provides a set of working guidelines for minimizing this problem, and helps explain both the historical preference for "old" oil, and for storing oil in the light for long periods of time. On drying, a film of hand refined organic (HRO) linseed oil aged in the light for three years does not yellow to a perceptible degree after eight months. The simple combination of a high quality, non-invasively refined oil with preheating or prolonged aging in the light may be a primary factor in the relative non-yellowing of older Low Country painting made with linseed oil. The oil forms a stronger paint film, is inherently more resistant to humidity, and does not yellow perceptibly over time.

Linseed Oil

While linseed oil has a recent reputation for yellowing, the linseed oil of Van Eyck, and of the Dutch painters of the 17th century has yellowed relatively little, if at all. Discussions about the generic behavior of linseed oil are confusing, because there are many different types of linseed oil. The focal issue is not the plant of origin, but the way the oil has been processed and refined. Quality here is paramount. While painters are always attracted to pale oil, the colour the oil starts out is not important, this is fugitive. If darkening occurs it is through the creation of hydroperoxides during polymerization: the "drying" which occurs through interaction with oxygen. It is possible to make an oil colourless using bleaching clay, as is consistently done with commercial oils, but this does not mean the oil will remain colourless over time. Wehlte points out thatit is natural to be drawn to the lightest oil, but a lighter oil may dry darker due to the way it has been processed. Cold-pressed linseed oil is considered more generally reliable than hot-pressed or alkali-refined linseed oil. But even if the oil is cold-pressed, there are variables. Factors such as growing climate, ripeness of the seeds when harvested, and the care which has been taken to exclude other seeds from the oil are all mentioned by Wehlte. When reading about test results on linseed oil, it is important to find out as much as possible about the oil with which the tests began, and how it was or wasn't processed. Using a quality cold-pressed, refined commercial linseed oil will alleviate much yellowing potential. This can be purchased from many of the older or higher quality paint manufacturers. It is at least moderately

expensive, but typically yellows minimally. However, this is at the price of a faster drying rate, because this oil has been so totally refined.

The thoroughness of the refining process also results in this oil losing much of the rheological potential inherent in linseed oil. It is safe, but has also been effectively stripped of its personality. With any commercial cold-pressed oil, the elements of the process are both involved and unknown outside the trade. This is an area where it is beneficial to be patient and do yellowing tests, as some of these oils will prove better than others. A show of technical responsibility is becoming a more prevalent as a marketing strategy, but may or may not in fact have a quality oil to back it up.

While the older texts contain endless different recipes for refining linseed oil to make it less yellowing, painters will occasionally become interested in unrefined linseed oil on the theory that it is somehow more pure or original, or that, in an era devoted to over-refining natural products, unrefined must be better. The long term problem is that the fatty acids in the oil do not polymerize, and become more acidic over time. An oil from which the fatty acids have been removed will produce a stronger paint film which is also less acidic and less reactive to the great potential issue of atmospheric moisture over time.

Experience has shown hand-refined linseed oil to be capable of a variety of rheologies and behaviors that modern linseed oil simply cannot emulate. This may explain why the "lost secret" has always been thought to be something outside the loop of well-known materials. The actual secret may have been hidden in plain sight all along in the oil itself. To refine linseed oil by any one of several traditional refining methods, please download Refining Linseed Oil.