

The Past and Future History of Natural Resins as Coating Materials in Conservation

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Abstract

Natural resins have been employed in a variety of fashions from the distant past to the present, most notably as transparent coating materials in creating and preserving cultural and artistic objects. Their availability, range of use and modification, and appearance, make natural resins well-suited for this purpose. In recent decades there has been a strong emphasis on finding additional options (e.g. synthetic resins) for materials used in the coating process for both craft and conservation.

Ostensibly this quest for new, substitute coatings is the search for "better" coating materials, and requires defining the desired characteristics for coating resins. Within that context, this paper discusses natural resins as coating materials, and in light of many disparate factors, their possible future use either as coating or modified coating materials, or as models or building blocks for synthetic resins to mimic their beneficial properties.

Introduction

Throughout most of the history of coating materials, the objective of their use has been to impart a glossy, durable surface to the object on which they are applied. It remains unclear at this late date what the early accounts meant exactly by the terms "glossy" or "durable" or any other desirable attributes, but it is certain that resinous materials, that is materials not softened by cold water, were used once they were found to impart desired characteristics to coatings. Regardless, it is only with the infatuation of the antique by the moderne that aesthetic preferences other than these began to take hold, as exhibited by the "antique" coatings and decorations employed with varying degrees of fashion in recent decades and centuries.

Much of the attempt to replicate the coatings of the ancients has been an effort to recapture the romantic notion of the craftsman using "natural" materials, which are by definition in this arena to be "more beautiful" than modern synthetics. There is an almost indescribable visual quality ("saturation," "sheen," or even "glow") to a coating of low-molecular weight natural resin as opposed to the "plasticky" appearance of modern high-molecular-weight synthetics. In reality, a skillful craftsman can render nearly any aesthetic in a wide variety of materials, natural or not. There remains, however, affection for the methods and materials of our

predecessors, and thus utility in our understanding of them as preservers of artifacts. And, as industry, commerce, and craft change at an ever-increasing pace, it remains incumbent upon us to define the usefulness of what we do, and the materials with which we do it.

But what of a "future history?" The challenge to the future of natural resins derives from three sources. First and second, inexorably linked in a cycle confounding any attempt to assign cause or effect, are the simultaneous increase in production and use of synthetic resins (that can be "tailor made", and whose production costs are in general declining) while the production of natural resins is threatened by the removal of the sources of the raw material from the marketplace. This is inevitable as integrated and local economies focus on more efficient means of increasing wealth, and as the need for different use of lands and forests becomes manifest. Some of these factors can be responded to, such as the merging of material technologies and chemical engineering of coatings, as natural resins can be the building block on which natural-synthetic hybrids can be derived. However, the coating industry is not likely to have an effective response to changes in population density that are, for example, removing from production much of the prime lac-harvesting territories in Indochina. But it is the third major factor that will, in my opinion, have the most profound effect on the coatings industry in the future, as it has for the last three decades -- the increased moratorium on vaporous organic compounds, most conveniently identified are organic solvents. In a world increasingly sensitive to the presence of "toxic" materials, we must either learn to understand and communicate about our materials, or lose their use through the edicts and decrees of environmental and industrial-hygiene regulations. Without this, and without the ability to understand the means to modify our coating materials, we could find ourselves in a scenario where the palette we have left won't paint the picture we want: in other words, there might not be a future history of natural resins or other solvent-borne synthetic substitutes.

Complicating these images are the factors inherent to our own discipline of conservation. We use natural resins only partly because they are what we have become familiar with. But are they the best material for what we do? That is a question without a clear "Yes" or "No" answer, because the question does not clarify what "best" means. Each coating material, including natural resins, has characteristics, some of which we call "good" and others "bad." A review of what we want our coating materials to do is integral to any discussion of their future in our work, for if they don't do what we want, any discussion of their "future" is moot.

Natural Resin Coating Materials

Generally natural resins are classified according to source, although there are very useful delineations based on the structure of the resin molecules. This paper will use the former, primarily because I am a craftsman first and a chemist second. Two broad classes of natural resins within the former are those derived from animal sources, and those derived from plants. There is only one meaningful animal-based resin, lac (or shellac), while there are dozens of vegetable or plant-based resins, including those harvested as fresh exudates (damars, balsams, etc.) and others that have become mineralized or fossilized (amber, copals). Inasmuch as there are numerous in-depth technical treatises on this subject, this paper will review them only

cursorily.

Damars

Damar is not a single resin, or even a particularly good designation for a group of resins. "Damar" is a word simply meaning "(burning) resin" to the Malaysian peoples who live in the regions where the materials originate. There are perhaps more than 500 species of tropical hardwood trees yielding "damar" resin. Like most natural resins, the use of damar predates any written records, as it has been used since antiquity as a fuel, coating, adhesive, or any other purpose its harvesters could develop.

Damar is a naturally occurring exudate harvested by "tapping" trees, collecting the sap from naturally wounds to the surface of the tree. as there are many differences to trees by species, location, or environment, there are also accompanying differences in the properties and characters of the resins themselves, which vary in hardness, clarity and color, and working properties. Usually made into a solution with oil-like solvents (turpentine, aromatic hydrocarbons) damar makes a widely used varnish for oil paintings, but its inherent instability requires it to be removed and replaced frequently.

Balsams

Balsams, much like damars, are the exudates of trees, in this case conifers. Coniferous exudates are usually a mixture of a volatile solvent-like component and a resin. During the refining process to separate them, the volatile portion is distilled into turpentine and light balsams, and the resins are the remains. In many cases the term balsam refers to a blend (or re-blend) of the two components, which are usually viscous liquids. Balsams come from nearly every area of the globe, with varying properties based on species and location.

Balsam resins include colophony, resin widely used as a cheaper substitute for better-quality resins. Colophony has a reputation as a poorly drying, sticky material that is in every way an inferior ingredient in varnish recipes. The problem of drying colophony could be addressed by using it in alcohol rather than turpentine or oil. Once dry, colophony is very brittle, yielding a darkened, fractured surface in only a few years.

Elemi is another balsam-type resin, very soft, and often used as a plasticizer or adhesion improving ingredient, although these effects may be short-lived. Sandarac, from a small north African conifer soluble primarily in alcohol, is a brittle resin generally considered by many to be unusable except in coatings with other materials.

Copals

Copals are also tree-exudate resins, some grades of which are partially or fully fossilized. Unlike damar resins, copals are root products, rather than bole or trunk products, and must usually be dug out of the ground. Mineralization of the exudate begins almost immediately, and more than anything else the degree of fossilization determines the properties of the resin.

The fresher the exudate, the softer the resin and the easier to introduce into solution, and the more fossilized, the harder and more difficult to make liquid. The purest, fully fossilized forms of resin are amber, which are nearly impossible to use as a varnish solution.

Grades or types of copal are defined by the areas of origin in addition to their fossil state. Congo copal is from central Africa, and often too hard or fossilized to use until it has been heated to such a degree that thermal breakdown of the structure occurs, after which it can be introduced into a hot oil solution. Manila copal, a much softer material, is soluble in alcohol without processing, and is therefore more widely used and available. Two other copals, Boea and Pontianak, must also undergo thermal degradation to be introduced into a delivery system.

Kauri, while not a true copal, is a fossilized balsam from New Zealand, and was widely used as an interior varnish following thermal processing.

Mastic

Mastic is derived from a small tree that grows on the rim of the Mediterranean, and was often used as a substitute for damar, although it is softer than the other resin. Mastic is considered to have excellent working qualities, being soluble in alcohol and available for use as a spirit varnish. Exceedingly pale in color, mastic is used when minimal color shift from the binder or varnish is desired, although it yellows badly once it begins to degrade. Perhaps most important for its continued use is that mastic remains very thermoplastic, and can be removed easily once it degrades or begins to darken.

Shellac

Lac is the name given to the natural resins which are of insect rather than vegetable origin. (In common usage such as 18th and 19th century varnisher's manuals lac came to mean any natural film-forming resin). The lac most familiar as furniture varnish is a thermoplastic resin refined from the secretions tiny insect Laccifer lacca, indigenous to Indochina and India. The exudate of the lac bug contains naturally occurring dye, wax, and resin.

There is no agreement as to the first use of shellac, or even if the use of the resin as a coating is contemporary with the use of lac dye. Reference to both the dye and the resin occur very early. In any case one of the earliest European visitors to the Orient in the late 1500's reported that shellac was widely used on household items of all kinds and provided a surface of high sheen.

The shellac trade between the Orient and Europe began at the beginning of the seventeenth century with the primary emphasis placed on the acquisition of lac dye as an inexpensive substitute for costly cochineal dye. The resin gained importance very slowly and did not achieve widespread use in the West for nearly two centuries. Shellac finishes on furniture became fashionable at the beginning of the 1800's and their popularity continued unabated until the development of synthetic resins, particularly cellulose nitrate lacquers.

The characteristics of lac-based varnishes depend greatly, based on the host tree for the insect, the harvest season and processing of the raw material, and preparation, use, and age of the solution. Generally the resin is placed into solution with one of the lower alcohols, or an alkali aqueous preparation.

Typical Uses of Coatings Materials

An evaluation of coating materials must include the variety of uses to which these materials are put but artisans and conservators, who employ film forming materials in a wide variety of ways: as isolation layers, painting and in-painting media, consolidants, and as final finishes. These categories are assigned according to the intended purpose of a particular project or technique, and the location of the material employed within the artifact surface. The term "surface" means not just the final interface between the object and the ambient environment, but also all areas visible to the viewer, or the "presentation surface." The term "coating system" is often used intentionally because only rarely is a single layer of one material applied to the surface of any particular artifact.

Isolation Layers: One of the underlying principles to conservation treatments is the ability of the conservator to leave some trace of their interaction, or intrusion, with the artifact, and to separate (distinguish) that intrusion from the pre-existing artifact as much as possible. To that end, isolation layers or barriers are used routinely to construct discrete laminar systems of surface treatment. Isolation layers protect original finish from in-paint and final finish. The effect is that of sandwiching visual modification between layers of isolating varnish.

Inpainting Media: Visual modification (necessary to compensate for damage to the presentation surface) is referred to as inpainting, an aesthetic modification which can include the application of opaque polychromy (true inpainting), the use of translucent pigmented or dyed resinous materials over large areas to provide a general, overall color shift (glazing or toning), and the modification of surface texture and buildup, and gloss. Virtually all of these methods employ film-forming materials, either as a stand-alone coating, or as a medium for the colorant or other modifier.

Consolidants: Consolidation is the encapsulation of materials in order to provide internal, mostly structural, integrity to the degraded artifact, e.g. adhere and strengthen weak wood, or in the case of the decorative surface, to stabilize a fragile and flaky finish. The degree to which consolidation of the surface is employed and successful depends on the nature of the coating being treated, and the properties of the consolidating material/technique.

Final Finishes: The final finish is indeed the top coating enclosing all the coating treatment aspects, protecting the physical materials providing the visual integration and giving it the desired overall appearance. It is more than a mere shrink wrapping of the object, it is the final step to a sometimes complex process unifying the visual interpretation of the object. This final step is every bit as vital as the previous ones, for a poorly applied or ill-chosen coating can substantially detract from the appearance of the artifact.

How Should Coating Materials "Behave"?

As we consider natural resin coatings, and our ability to change and manipulate them, the list describing their perfect behavior appears as a manifestation of wishful thinking, or at least mutually exclusive desires. The properties can be organized under general topics: ease of application, chemical stability, moisture permeability, toughness, hardness, light transmission, dimensional stability, inertness, and visual properties.

Ease of Application: The resin should be soluble in easily obtained solvents (preferably those which do not affect existing coatings), lend itself to either spray or brush application, and form films quickly at room temperature. If the coating is a dispersion, it should have a low film formation temperature.

Chemical Stability: The properties should remain the same for the life of the coating; the resin should be resistant to chain scission, cross-linking and chemical changes. Its solubility should not change, keeping it easily removable in solvents which will not disturb underlying coatings.

Moisture Permeability: The coating must be a good moisture barrier. A good moisture barrier can be used to protect the wood from fluctuations in the relative humidity, limiting expansion and contraction which can damage both wood and coating. A good moisture barrier will also protect original coatings which can soften or become cloudy in the presence of moisture.

Toughness: The coating must be able to withstand small amounts of stretching and compression due to wood movement; also, it should not be so brittle as to shatter upon light impacts. This can be accomplished by addition of plasticizers, but most such additives can migrate or be leached out in time.

Hardness: The film should not be so soft as to be easily scratched or to pick up and imbibe dirt. Obviously, this property is in opposition to that of toughness, and the two must be balanced. For dispersions, this property is also in opposition with the low film formation temperature requirement; the resin must have a low enough glass transition temperature to coalesce, but then not be sticky as a formed film.

Light Transmission: The coating should filter or block UV, to protect the underlying wood and coatings. Although this can be accomplished with additives, a UV absorbing film would be ideal. Additionally, the coating should not be yellow or otherwise colored.

Dimensional Stability: The dried film should not shrink when drying or upon aging.

Inertness: The coating should not produce or exude harmful chemicals; acidic degradation products or reactive migratory additives will cause undesirable changes in neighboring materials.

Visual Properties: The coating should be capable of excellent surface saturation (mostly a

function of low viscosity at high concentrations), clear, and manipulable in regard to gloss. This last is important when the appearance of an existing coating is to be matched; a very glossy finish is often undesirable.

Which of the natural resins possess the previous list of attributes? It is a nonsensical question, for none possesses more than a few. Given this reality, do we still believe natural resins are still important to us? If the answer is yes, then as suggested in the Introduction, we as conservators must take an active role in the continued development of coatings containing or based on natural resins.

Looking to the Future

Clearly no one resin is "perfect" for every application. However, artisans conservators choose from a broad range of materials in a variety of formulations to obtain satisfactory results for specific purposes. Some of these formulations have not changed much in recent years, and we are not taking full advantage of more recent research on new materials and formulations.

Conservators generally rely on professionals in other disciplines to design their products. Most of the coatings used in the conservation were developed for use in outdoor paints or floor and automotive finishes. Because conservators do not use great quantities of these materials, conservation will never influence large-scale research or production.

Suppliers and producers of natural resins might change availability and formulation in the future, especially as industrial needs change. For example, even though a conservator might be waived from compliance to low volatile organic compounds (VOC) regulations, the solvent-based natural resin products he uses might become unavailable as the markets shift to comply with regulations, or the manufacturer may produce the same film former in a delivery system unacceptable to us.

I am convinced that for natural resins to remain a viable option for conservators and artisans, we will have to contribute to a variety of ventures essentially foreign to us. First, as industry veers further away from using natural resins in any way, we must work together and with specific corporate partners to assure that there will be at least some supply of the raw material. For without the raw material, without the harvesting in Malaysia, without the processing in Indochina, and the shipping overseas, there is no natural resin to use in varnishes in Paris, London, San Francisco, or Tokyo. If industrial need for natural resins evaporates, so will their supply.

Second, we must continue to explore the use of natural resins in concert with compatible synthetic film forming materials. Many synthetics have very desirable qualities, as do natural resins. Selecting and creating blends of varied materials to both extend desirable properties (e.g. appearance) and impart new ones (e.g. chemical stability) is a logical first step once the natural resin takes up residence in your studio. This will require an increased understanding of the behavior of film forming materials, whether natural or synthetic, in solution and in film. It will likely lead us to work at the periphery of solubilities, as, for example, in the blending

of shellac with Acryloid B-67.

Third, we must develop our own formulations of natural resin coatings based on reduced organic solvent portions to comply with new and increasingly stringent environmental regulations. The agenda for reducing VOC's will not, in my opinion, be substantially altered in the immediate future. Conservators and artisans will have to move to new product formulations along with the rest. As the typical use of a coating can be varied, the new coating delivery systems will need to be versatile. A person choosing or describing these products (or a manufacturer trying to assist in this choice) will need to take into account first the way the coatings are used and generate the "wish list" of desired properties, then attempt to fulfill the wishes. In many respects this is the most difficult task, taking the working properties of a film-forming solution, and trying to replicate those same properties in a film-forming emulsion, or other delivery system type, while recognizing the difficulties of creating complex and unstable mixtures. The ideal coating would use minimal additives, to minimize the risk of changes in the coating with time as the additives migrate, or changes in neighboring materials as a result of contamination.

And finally, since the large-scale availability of natural resins cannot be assured, we must explore alterations to resins to make them more durable, and thus in need of replacement less often. This can be accomplished through the use of many stabilizing compounds such as UV absorbers, antioxidants, and hindered amine light stabilizers. Much more work needs to be conducted to investigate the efficacy of these materials, and the development of more efficient synthetic additives. An even more ambitious effort would include the creation of new molecules based on natural resin structures and raw materials, resulting in integrated materials with custom-made properties.

Conclusions

Future natural resin coatings should utilize a resin/polymer/additive blend which best fits the above wish list. Currently, acrylics are considered to be the most stable synthetics for this purpose, and they are manufactured in a broad range of properties. The incorporation of polymer-bound UV absorbers, plasticizers and stabilizers can further improve formulations for this field.

A broad variety of coatings, natural or synthetic will address the solubility issue: ideally, a conservation coating's solvent should not swell or dissolve any original materials on an artifact. Because the composition of artifacts changes from piece to piece, conservators need a selection of resins having different solubility parameters.

The future of conservation coatings, then, lies in utilizing and building on advances made for commercial coatings. As the availability of currently used coatings changes, the conservation field will need to compare new coatings with the above wish list, and consider which, if any, can be adapted. In some cases, small specialty suppliers might be an answer; conservators could then use materials and formulations made specifically for their applications, rather than trying to fit existing products to their needs.

General References

Barry, T. 1932. *Natural Varnish Resins*. London: Ernest Benn.

Barry, T. and G. Duncan. 1934. *Varnish Making*. London: Leonard Hill Ltd.

de la Rie, R. New synthetic resins for picture varnishes. In Mills, et al, eds. *Cleaning, Retouching and Coatings*, Preprints of the Contributions to the Brussels Congress, 3 - 7 September 1990. London: IIC.

----- The chemistry of ketone resins and the synthesis of a derivative with increased stability and flexibility. *Studies in Conservation*, **34**, 9-19.

-----The influence of varnishes on the appearance of paintings. *Studies in Conservation*, **32**, 1-13.

-----Polymer Stabilizers. *Studies in Conservation*, **33(1)**, 9-22.

----- and C. McGlinchey. Stabilized Dammar Picture Varnish. *Studies in Conservation*, **34(3)**, 137-146.

Hansen, C. Three Dimensional Solubility Parameter - Key to Paint Component Affinities. *The Journal of Paint Technology*, **39(505)**, 104-117.

Hedley, G. Solubility Parameters and Varnish Removal: A Survey. *The Conservator*, **4**, 12-18.

Hess, M. 1965. *Paint Film Defects - Their Causes and Cure*. Chatham, U.K.: W & J MacKay and Company Ltd.

Howes, F. 1949. *Vegetable Gums and Resins*. Waltham, Mass: Chronica Botanica.

Jolly, A. A Hundred Years of Resins. *Polymers Paint and Colour Journal*, **May 30, 1979**, 514-515.

Koller, M., and F. Mairinger. Problems of Varnishes: Use, Appearance and Possibilities of Examination. In: *ICOM Committee for Conservation 4th Triennial Meeting*, **1975**, 75/22/9.1-9.

Lomax, S., and S. Fisher. An investigation of the removability of naturally aged synthetic picture varnishes. *Journal of the American Institute for Conservation*, **29(2)**, 181-192.

Mantell, C., et al. 1942. *The Technology of Natural Resins*. New York: John H. Wiley.

Martens, C., et al. 1968. *Technology of Paints, Varnishes and Lacquers*. Malabar, FL:

Robert E. Krieger Publishers.

Masschelein-Kleiner, L. 1985. *Ancient Binding Media, Varnishes and Adhesives*. Rome: ICCROM.

Mattiello, J., et al. 1943. *Protective and Decorative Coatings, Volume I - Raw Materials for Varnishes and Vehicles*. New York: John Wiley.

Mills, J., and R. White. 1987. *The Organic Chemistry of Museum Objects*. London: Butterworths.

Penn, T. Decorative and Protective Finishes, 1750-1850: Materials, Process, Craft. *APT Bulletin*, **XVI(1)** 3-45.

Sengupta, S. et al. Modification of Shellac. *J. Oil color Chemists Association*, **63**, 15-22.

Teas, J. Graphic Analysis of Resin Solubilities. *The Journal of Paint Technology*, **40(516)**, 19-25.

Stalker and Parker. 1961. *A Treatise on Japanning and Varnishing (1688)*. London: Alec Tiranti.

Williams, D. Shellac Finishing. *Fine Woodworking*, **71**, 56-59.

For a much more thorough bibliography on natural and synthetic resins, coatings technology, deterioration and restoration, contact the author.