

Archaeological Preservation Research Laboratory Report 18:

**Polymerization of PR-10, PR-12 and PR-14 Silicone Oils In Animal Hides Using Catalyst Fumes - Keratin and Amino Acid Cross Linking**

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In an experiment conducted at the Conservation Research Laboratory entitled "Shoe Experiment - Consolidation of Old Leather Using Silicone Oils," a pair of old shoes, whose surfaces had become cracked and crazed due to drying and loss of natural oils, was revitalized using silicone oils and CT-32 catalyst. No crosslinking agent was used during the process. At the time of the experiment, no identification or definitive testing was conducted on the conserved shoe to determine what chemical or combination of conditions acted to cause the crosslinking and polymerization of the silicone oil that was added to the leather, even though the shoe was perfectly preserved. This experiment has been devised to test the possibility that silicone oils may be polymerized to some degree without the aid of a crosslinking agent.

For this experiment, three molecular weights of Dow Corning Corporation silicone oils were mixed with untreated, dried horse hide and placed in 2-, 4- and 8 gram samples sizes for curation in the fumes of CT-32 catalyst. Sodium hydroxide was added, in the amount of 4% by weight, to samples 9 and 10 before exposure to CT-32 catalyst fumes. These two samples were included to determine the effect of sodium hydroxide on the polymerization of silicone oils. This information is invaluable for marine archaeological conservation because many artifacts that are recovered from marine excavations are stored in a caustic soda solution before prior to conservation. Sample combinations and sizes are listed in Table 1 below:

<b>Sample</b>	<b>Molecular Weight Silicone oil</b>	<b>Sample Size (g)</b>	<b>Catalyst</b>
<b>1</b>	<b>PR-10</b>	<b>2</b>	<b>CT-32 fumes</b>
<b>2</b>	<b>PR-10</b>	<b>4</b>	<b>CT-32 fumes</b>
<b>3</b>	<b>PR-10</b>	<b>8</b>	<b>CT-32 fumes</b>
<b>4</b>	<b>PR-12</b>	<b>2</b>	<b>CT-32 fumes</b>
<b>5</b>	<b>PR-12</b>	<b>4</b>	<b>CT-32 fumes</b>
<b>6</b>	<b>PR-12</b>	<b>8</b>	<b>CT-32 fumes</b>
<b>7</b>	<b>PR-14</b>	<b>4</b>	<b>CT-32 fumes</b>
<b>8</b>	<b>PR-14</b>	<b>8</b>	<b>CT-32 fumes</b>
<b>9</b>	<b>PR-10</b>	<b>4</b>	<b>NaOH-CT-32 fumes</b>
<b>10</b>	<b>PR-14</b>	<b>8</b>	<b>NaOH-CT-32 fumes</b>

Table 1. Samples included in this experiment.

#### Procedures

As a means of testing the polymerization potential of various weights of silicone oil, a large section of fresh horse hide, measuring approximately 36 centimeters square, was washed in several rinses of running water. A sharp knife was then used to remove as much of the sub-cutaneous flesh from the hide as possible. After de-fleshing, the hide was placed back into a fresh water rinse where it was allowed to sit for several hours. Several new disposable razors were used to shave the hairs from the surface of the hide and the hide was rinsed one more time after shaving. After thorough rinsing, the hide was placed into a large container with 1 liter of fresh ethanol and allowed to dehydrate at room temperature for 24 hours. After initial dehydration using ethanol, the hide was moved to a large glass jar containing 1 liter of acetone. While in this solution, the hide was placed into a freezer mounted vacuum chamber and a vacuum of 170 microns was applied for six hours. After vacuum dehydration, the hide was allowed to sit in solution in the freezer for an additional twelve hours to ensure that the water-acetone exchange was

complete. After thorough dehydration, the hide was tacked to a large board using push pin tacks and allowed to dry out at room temperature for 48 hours.

Once dried, the hide was folded in half several times, forming a hard clump of dried leather. In this state, the hide was easily flaked into small particles which could be mixed with silicone oils to determine the range of effects and degree of polymerization which might occur among the oils of different molecular weight. Hide dust was mixed with each of the three main silicone oils to form a thick paste. This step was accomplished without measuring the proportion of hide to silicone oil because it was determined that enough hide dust would be added to each silicone oil to create a thick paste. Once each paste solutions were ready, 2-, 4- and 8 gram samples of each of the three molecular weights of silicone oil/hide solution were placed into small flat trays. Additionally, one sample each of the PR-10 and PR-14 silicone oil/hide solutions was poured into a similar flat tray; several grains of sodium hydroxide were added to these solutions and, after mixing, the samples were included with the hide samples for additional testing.

All of the samples were placed into a large containment chamber which had a tight-fitting base as well as hose port attached to it so that catalyst fumes could be pumped into the chamber. The chamber was placed into a large warming oven that had been preheated to 57°C. Sixty ml of CT-32 catalyst was placed into a clean flask and then attached to a support stand with a heat lamp directed below it. Two hoses were attached to the flask. One hose was used to connect the containment chamber to the flask and the other hose was used to pump air into the flask via a small air pump. The heating lamp was used to heat the catalyst to the point that vapors appeared on the sides of the flask. An air pump was then used to divert the catalyst fumes into the containment chamber where they came in contact with the surfaces of the silicone oil/hide samples (Figure 1). All samples were treated in this environment for 12 hours. At this time, all of the samples were evaluated and then returned to the containment chamber for an additional twelve hours of treatment. After exposure to catalyst fumes, all of the samples were removed from the warming oven and allowed to sit at room temperature. After an additional 24 hours, the viscosity and other physical attributes of all of the samples was re-evaluated and recorded.

### Observations

Because of the freshness of the hide, de-fleshing was an easy task. Shaving the hide however, was extremely difficult. In spite of the care taken to remove hair from the hide before treatment, some small hairs were noted in the silicone oils during the mixing process. These hairs were removed using tweezers when possible. The addition of hide particles to each of the molecular weights of silicone oil was a task that was best accomplished in stages, adding additional hide to each of the silicone oils slowly as a means of matching texture and consistency between the three silicone oils being tested.

An almost instantaneous reaction was noted when sodium hydroxide was added to samples 9 and 10. Approximately fifteen grains, each about the size of a grain of salt, were added to the two samples and small white bubbles were noted in each of the

samples during the mixing process. After two minutes of mixing, the viscosity of sample 10 was noticeably thicker, although the samples never completely hardened.

Apart from samples 9 and 10, chemical reactions for each of the other samples was considerably slower. After twelve hours of curation, visible silicone oils in sample 1 had turned slightly cloudy in coloration with small thickened clumps surrounding the masses of shredded hairs. At this point, a very small quantity of clear surface liquid was noted on the sample. After thirty-six hours of curation, the viscosity of the sample had increased substantially and there were visible clumps of solid silicone surrounding strands of hair extending from the sample. While these hardened areas suggest that there were areas where total polymerization had occurred within the sample, the sample was generally determined to be a stiff paste.

Like sample 1, visible silicone oil associated with sample 2 turned cloudy after twelve hours of curation. Areas of clumpy hair were observed in this sample and the sample was less viscous than sample 1. After thirty-six hours of curation, the viscosity of the sample had increased greatly, although sample 2 still remained less viscous than sample 1. Sample 3 also contained indications of hardening clumps associated with the hair in the sample; after thirty-six hours of curation, the sample was runny and less viscous than sample 1.

Sample 4, which consisted of a two-gram sample of PR-12 and ground hide, exhibited many of the same changes in color and viscosity as sample 1. After twelve hours of curation, the sample had thickened substantially; after thirty-six hours, viscosity and polymerization had increased to the point that the sample had taken on the consistency of an extremely thick paste. Like sample 4, sample 5 had increased in viscosity after twelve hours of curation, but after thirty-six hours of curation, the sample was not as viscous as sample 4. Similarly, after thirty-six hours of curation, sample 6 had formed into a relatively thin paste as compared to sample 4.

Similar to the PR-10 and PR-12 silicone/hide compounds, the heavier molecular weight PR-14 silicone oil/hide solution showed the same trend towards increased viscosity in smaller sample sizes. After thirty-six hours of curation, sample 7 had indeed become more viscous but never to a point comparable to sample 5. Sample 8, which was an eight gram sample, was thinner in viscosity than sample 7 and substantially less firm than sample 5. Data regarding the twelve- and thirty-six hour observations of all of the samples are listed in Table 2.

Table 2 Sample Observations

<b>Sample No.</b>	<b>Silicone Oil</b>	<b>12 hours</b>	<b>36 hours</b>
<b>1</b>	<b>PR-10</b>	-some hair clumps -solid -some runny fluids	-clumps bigger -generally more solid
<b>2</b>	<b>PR-10</b>	-some clumps -runny compared to #1	-thickened clumps around hairs -thickened but runny compared to #1
<b>3</b>	<b>PR-10</b>	-some clumps -some thickening	-thicker -not as thick as #1
<b>4</b>	<b>PR-12</b>	-thickened -some clumps noted	-thick but not solid
<b>5</b>	<b>PR-12</b>	-thickened -some clumps noted	-thickened to a paste
<b>6</b>	<b>PR-12</b>	-thickened slightly -some clumps noted	-thin paste
<b>7</b>	<b>PR-14</b>	-some thickening -not as thick as #3	-thin paste -not as thick as #5
<b>8</b>	<b>PR-14</b>	-some thickening -not as thick as #3	-thin paste -thinner than #7
<b>9</b>	<b>PR-10</b>	-thickened -bubbles and white solids noted	-very thick -some hard clumps
<b>10</b>	<b>PR-14</b>	-thicker than #9 -bubbles and white solids noted	-very thick with hard bottom

Because of the inherent differences in viscosity between the three silicone oils used in this experiment, assessment of the changes in viscosity were difficult and the samples were ultimately evaluated as groups.

## Conclusions

Although only a small number of samples were used for this experiment, several conclusions can be made about the nature of the combination of silicone oils and hides and their ultimate preservation in the presence of catalyst fumes. For all three molecular weights of silicone oils, the trend towards a greater change in viscosity in the smaller sample ranges suggests a correlation between viscosity and sample size. In all cases, the thinner, smaller samples appeared to have increased more in viscosity than the larger, and therefore thicker, samples. This suggests that either the surface of the samples was reacting with catalyst fumes and preventing the silicone oils located at greater depths within the sample trays from polymerizing, or that the catalyst was exhausted from either heat or oxidation before the greater depths of the samples had been effected. In either case, polymerization as the result of entropic reaction appears to have been minimal in these samples.

Our research has indicated that the hide itself may contain some of the necessary components to cause subtle crosslinking when in contact with silicone oils and catalytic agents. In an experiment which was reported in the Journal of the Society of Leather Technologists and Chemists (Volume 66, 1982). Discussing the nature of collagenous connective tissues, E. Heidemann reported that "hides become insoluble by the process of natural crosslinking alone" (Heidemann, 1982: 21). He also noted that "cross-linkages therefore lead to the formation of the profile-like so-called linkage regions." Although the focus of his studies was to determine the impact of crosslinking potential as it applied to chrome tanning processes, his observations are similar to those made in this paper. Although the hair was removed from the hide prior to contact with the silicone oils, the hair follicles also contain keratin and a host of amino acid compounds in the form of proteins in polypeptide chains. Crosslinking can occur in a substance made of polypeptide chains as the result of the disulfide bonds of cysteine residue which is found in keratins. Insulin and other proteins can also support this crosslinking mechanism.

The ramifications of natural crosslinking agents that are found in keratin and amino acid N-carboxy-anhydride rich organic materials, such as untreated animal hides and feathers, is wide-ranging. Numerous industries associated with animal husbandry and the preparation of animal hides and feather products could undoubtedly profit from the research and development of these natural crosslinking agents. Genetic manipulation and selective breeding for increased hair follicles may also heighten the potential for hide preparation using silicone bulking technologies.

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Citation Information:

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