Pemulen

For the past few years, a small number of conservators have been following Richard Wolbers' lead and experimenting with Pemulen, a poly acrylic acid similar to Carbopol. Pemulen holds the promise of resolving many cleaning issues in conservation. Pemulen based emulsion systems can solve vexing problems that require both aqueous and solvent components simultaneously. They can sometimes replace simple solvent cleaning systems, reducing the amount of solvent needed dramatically and minimizing the conservator's exposure to hazardous fumes.

As yet, while we have a fundamental understanding of how it works, how it can be used in conservation, remains a bit elusive. One problem is that there are so many options for building a cleaning system (pH, inclusion of chelating agents, inclusion of surfactants, amount and choice of solvent to emulsify) it's difficult to feel one has a sense of how it will work on a given problem.

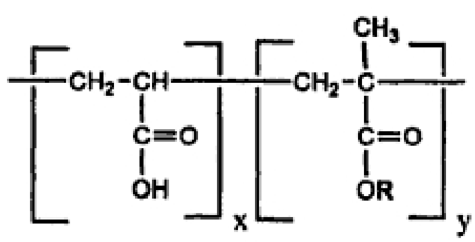
This collection of short articles and case studies is intended as an introduction. First, a short description of its chemical structure and behavior, followed by case studies which describe its use as a part of treatment, and last a primer on integrating Pemulen into the MCP, with a batch of recipes.

Pemulen, like the Carbopols, is made by Lubrizol (formerly Noveon). Small amounts can be purchased from "The Personal Formulator" <http://www.personalformulator.com/wvss/>. There are two grades, Pemulen TR-1 which holds up to 20% "oil" in an emulsion, and Pemulen TR-2 which holds up to 50%. Because of the versatility of the greater emulsification power, everyone in conservation has been experimenting with the Pemulen TR-2.

Pemulen® TR-2: An Emulsifying Agent with Promise

by Nancie Ravenel

Pemulen® TR-2 is a polymeric emulsifier introduced in the late 1980s by B.F. Goodrich and now produced by Noveon, a subsidiary of Lubrizol. In the cosmetic industry literature, Pemulen TR-2 is part of a class of copolymers referred to as acrylate/C10-30 alkyl acrylate cross polymers (Goddard 1999) .



R = long chain alkyl group

It consists of a poly acrylic acid similar to the Carbopol® resins, cross-linked with a long-chained methacrylate. Thus, this polymer has lipohipllic regions (the methacrylate) as well as hydrophillic regions (the acrylic acid).

These regions of differing affinity allow Pemulen TR-2 to act as a primary emulsifier, that is, it can be used to make oil in water (O/W) emulsions without the addition of soap or surfactant.

Pemulen TR-2 does not form emulsions in the same way that traditional surfactants do. To produce an oil in water emulsion, a traditional surfactant surrounds a droplet of oil to keep it suspended in oil. Nonionic surfactants used for cleaning painted surfaces might be used in concentrations as high as 30% to form a macroemulsion (Wolbers 2000).

In contrast, Pemulen TR-2 can form stable O/W emulsions in as small a concentration as 0.4% (Noveon 1999), binding to the oil droplets with the lipophilic portions of the polymer chain that forms the gel. Therefore, emulsions can be built with far less surfactant than with more traditionally used materials. For instance, emulsions created in the conservation lab at Shelburne Museum contain Pemulen TR-2 in a 1% concentration in the gel.

Gels made with Pemulen TR-2 are most viscous in the pH range of 5-9. A range of alkaline materials are suggested by the manufacturer to formulate aqueous gels using Pemulen TR-2, including sodium hydroxide, ammonium hydroxide, triethanolamine (TEA), and Ethomeen C-25 (Noveon 2009).

One interesting feature of Pemulen is that this emulsifying agent is designed to break when the gel is in contact with a salt concentration similar to what one would find on human skin (Lubrizol 2008). This characteristic is desirable in the cosmetics industry where moisturizers need to be quickly delivered and absorbed into the user's skin, but less desirable in an emulsion designed to clean works of art. In practice, this breakage of the emulsion has been observed when attempting to clean very grimy areas and when the gel is left to dwell for an extended period.

Since the structure of Pemulen is described as being similar to that of Carbopol, it is assumed that clearance issues for Pemulen TR-2 would be similar to Carbopol. Thus, one could look to the solvent gel research undertaken at the Getty Conservation Institute(Dorge 2004) to be indicative of issues one might encounter when trying to clear an emulsion containing Pemulen TR-2. For the Carbopol gelling agents, clearance largely is related to porosity ofthe substrate being cleaned (Khandekar 2004).

Case Study 1. Dentzel carousel panels

Richard Wolbers introduced Pemulen TR-2 to the conservators at Shelburne Museum in his capacity of consultant to a 2007 IMLS-funded project to clean paintings on canvas from the museum's 1902 Dentzel carousel.

Eleven large paintings, measuring 8 ft. x 4 ft., surround the carousel's working mechanism. These panels had been unevenly coated with what is assumed to be a spar varnish which had yellowed with age. As well, machine oil had splattered the reverse side of the canvas and migrated through fissures in the paint and varnish to the top surface. Machine oil was also noted on the front of some of the panels, most likely from an engine which drove the carousel's organ.

Despite being more than 50 years old, the splattered oil had not completely cross-linked and continued to migrate into materials surrounding the panels in storage. Additionally, drips of lubricating oil from the overhead beams also marked the paintings. These oily drips had shrunken, hardened, and were pulling the underlying paint from the canvas.

Sixteen smaller paintings, measuring 6 ft. x 4 ft.,were located just under the radiating arms at the top of the carousel. They were coated with the same tough yellowed varnish. While these canvases were not stained with machine oil, occasional black drips of the lubricating oil were found on these panels.

Over the two day consultancy, Richard tested a number of cleaning methods, including free solvents, solvent mixtures, and Carbopol-thickened solvent gels. He also tried emulsions of benzyl alcohol in a gel made with Pemulen TR-2, triethanolamine (TEA), and deionized water. Emulsions were applied and agitated on the surface with a brush. The emulsion was wiped from the surface with a dry cotton swab, and the surface was rinsed with deionized water on a cotton swab.

Initial solvent tests on the varnish indicated that the it was slowly soluble in acetone. After a more complete battery of cleaning tests, the most effective systems to remove the yellowed varnish tested were:

- benzyl alcohol gelled with Carbopol, followed by a rinse of 1:1 petroleum benzine and isopropanol;
- 20% benzyl alcohol in deionized water gelled with Pemulen TR-2 adjusted to a pH between 7 and 7.5 with TEA, followed by a rinse with deionized water.

The splattered oil could be readily picked up from the surface using xylene on cotton swabs, less so using petroleum distillates on cotton swabs. We found that the 20% benzyl alcohol / Pemulen TR-2 gel adjusted to a pH of 7.5-8 was effective at removing both the black machine oil and the yellowed varnish.

As testing progressed, this emulsion proved to be too aggressive over the red and green colored paints. Richard suggested replacing the TEA with a 1:1 combination of TEA and a 2% solution of Tris(hydroxymethyl)aminomethane (TRIS) to create a less aggressive gel. At a pH of 7.5 this gel was effective at removing the discolored varnish and the machine oil, but did not disurb the paint.

In fact, an emulsion prepared with TRIS but no TEA was ineffective at removing either the oil or the varnish.

A further refinement of the process was suggested by paintings conservator Chris Stravroudis (2009). Rather than mixing a single Pemulen gel using a mixture of TEA and TRIS, Chris suggested making two gels at the same pH, one mixed with TEA, the other mixed with TRIS at the same pH. The two gels could be mixed by volume to easily build gels and emulsions containing a range of TEA concentration.

We chose to continue to use the Pemulen emulsions because in using them, we were using less organic solvent to clean the panels.

One of the panels before treatment. After treatment.

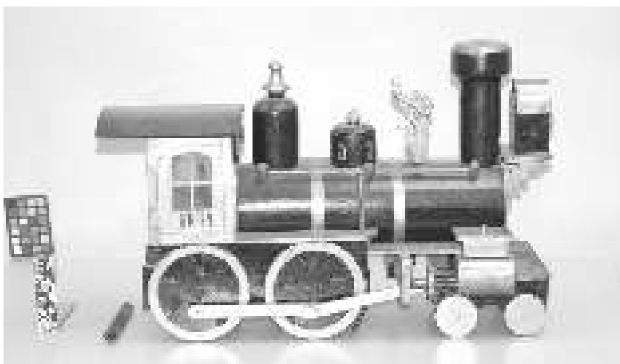
Gustav Dentzel Company, carousel panel depicting a woman walking a dog, 1902. Oil on canvas. Collection of Shelburne Museum, FC-7.62.

Pemulen® TR-2: An Emulsifying Agent with Promise, continued

Case Study 2. A miniature train engine

Admittedly, even though I find emulsions made using Pemulen TR2 to be quite useful for removing linseed oil coatings from painted surfaces, they aren't necessarily the first thing I reach for when considering cleaning options. I continue to test more traditional aqueous and solvent cleaning agents before trying gelled or emulsified solutions.

Towards the end of the IMLS carousel panel project, I was asked to remove a dirty wax coating from the painted wood surfaces of a folk art miniature train engine. The horizontal surfaces of the train were matte and grey with dirt, the vertical surfaces were black and glossy.



Before treatment, Francis Herbert Chapman, Model Train Engine, c. 1875. Painted wood, painted metal. Collection of Shelburne Museum, 1977-45.

A solution of 2% triammonium citrate in deionized water only beaded up on the waxy surface. Mineral spirits seemed somewhat effective, removing dirt but leaving behind a matte grey residue. More grime could be removed by alternating applications of mineral spirits with triammonium citrate, but the surfaces still appeared matte after cleaning. My next step typically would be to make an emulsion using a non-ionic surfactant such as Triton XL-80N. Instead I tried a Pemulen TR-2 emulsion made with mineral spirits.

The emulsion consisted of 1 g. Pemulen TR-2, 100 mL deionized water, 7.5 mL 2% TRIS, and 2.5 mL TEA, shaken with 10 mL mineral spirits. The emulsion was applied, agitated with a brush for about 10 seconds, removed with a dry cotton swab, and area rinsed with deionized water. The emulsion removed the dirt, and the area that was tested appeared as glossy as the engine's vertical surfaces after rinsing.

Cleaning tests on the engine's roof.

Conclusions

Although we've been working with Pemulen TR-2 aqueous gels and emulsions for a few years now at Shelburne Museum, questions remain in my mind about how it works. TEA plays multiple roles within the gel and emulsion: it neutralizes the acrylic acid/acrylate copolymer, it buffers the solution, and it also is active in the cleaning action. In projects where we have tested Pemulen TR-2 emulsions, it seems that the concentration of TEA in the solution plays a greater role in the amount of solvent added to the emulsion, but I have yet to explore this systematically.

Summer interns working at Shelburne Museum to remove linseed oil applied to carousel animals more than 50 years ago have successfully used aqueous gels mixed with Pemulen TR-2 and TEA where aqueous gels mixed with Carbopol, TEA, and citric acid were not as effective. Product literature from the manufacturers indicates that Pemulen is able to emulsify linseed oil and tung oil. Is Pemulen's ability to emulsify oil playing a role in this cleaning process?

As our interns and I continue to explore this emulsifying agent with promise, I am recording our methods and observations in a wiki, http://pemulentr2.pbwiki.com. Please consider yourselves invited to comment or share your own experiences using Pemulen TR-2.

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