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Treatment Options for Oil Stains on Paper

ABSTRACT

Oil stains on paper can be disfiguring and resistant to treatment. This study compares treatments involving solvents, enzymes, surfactants, and bleaches that paper conservators have reported to be successful.

Nine immersion treatments and sixteen local treatments were chosen for evaluation. Three questions were posed at the beginning of the study: (1) Which solutions or solvents are the safest and most effective in reducing oil stains? (2) Is it important to identify the oil before treatment, or are there certain reagents that will break up and solubilize any oil? (3) Is it necessary to consider the composition of the paper before choosing the appropriate treatment?

A sample population was prepared employing five types of paper, four types of oil, and three approaches to aging. Colorimetric data was collected and visual observations noted in order to determine the most effective treatment procedures.

INTRODUCTION

Oil stains can be transferred to works of art on paper through handling, a spill, or close contact with an oily object or media. The paper becomes not only discolored in the stained area but also less absorbent and more transparent as molecules of oil fill the spaces between cellulose fibers. In some cases, it is not desirable to reduce these stains because they represent artist's intent or historical evidence, or the treatment might affect nearby media. In other cases, lightening these stains is necessary for the aesthetic appreciation and understanding of the object.

OILS

Oils belong to the class of chemicals called esters and the subgroup called lipids. Each oil is a mixture of triglycerides, which are composed of a glycerol molecule with ester linkages to three long-chain fatty acids. Fatty acids are straight-chain hydrocarbons with a carboxyl group at one end. It is at this group that the ester linkage forms. The fatty acid can be saturated, meaning that there are no double bonds between the carbons; monounsaturated, containing a single double bond somewhere on the molecule; or polyunsaturated, containing more than one double bond.

Most oils are composed of several different fatty acids, each with an even number of carbons. Any combination of three fatty acids can link up with glycerol to make a triglyceride, also called a triacylglycerol. The amounts and types of fatty acids can vary not only between different types of oil, but also among samples of the same kind of oil. The exact composition depends on many factors of its production, such as the climate or soil where the source plant was grown and the method of extraction or expression used, but every oil has a general fatty acid distribution that determines its particular properties (Jamieson 1932).[1]

Double-bonded carbons are the primary components of the molecular structure of oils responsible for the yellow-brown color. The number of double bonds can be calculated from the amount of iodine that will react with a molecule at its double bonds. This calculation is called the iodine number of the oil, which is given as a range rather than an exact number (table 1).[2] To test whether the color of a stain directly corresponds to the iodine number, strips of Whatman filter paper were stained with drops of twelve different oils, aged two years in a window, and lined up by iodine number. There was a direct correlation between relative color and iodine number for every oil with the exception of poppyseed oil, which was very light despite an iodine number range of 140–158. It has been suggested that quinoid structures in oils with high linolenic acid con-

tent are also responsible for yellowing (Mills and White 1994, 40) and poppyseed oil has less of this fatty acid compared to other drying oils (Mayer 1981, 126). The presence of pigment compounds such as carotin, xanthophyll, and chlorophyll can also affect the color of the oil (Hamilton and Rossell 1986).

Highly unsaturated oils, which contain oleic or linolenic fatty acids, can form a solid film called linoxyn through oxidation and hydrolysis at double bond sites and are called drying oils. The oils with a moderate amount of double bonds are called semi-drying while oils with a low number of double bonds (a high number of saturated fatty acids) are nondrying. Vegetable oils, most of which are obtained from seeds, range in iodine number from low to very high (McNair 1929). They can contain small amounts of many other compounds, including free fatty acids, sterols, esters, phosphatides, vegetable extractives, waxes, resins, vitamins, and essential oils, that impart flavor and scent (Hamilton and Rossell 1986; Mills and White 1994). Mineral oils are derived from petroleum and have very low iodine numbers. Animal-based oils have low to moderate iodine numbers. Some animal and vegetable oils are solid at room temperature, and are called fats.

Four oils were chosen for testing: (1) linseed oil, a drying vegetable oil; (2) sesame oil, a semi-drying vegetable oil; (3) olive oil, a nondrying vegetable oil; and (4) bacon fat, an animal fat.[3]

PAPERS

Five papers of varying properties were chosen for testing in order to compare the efficacy of different treatments on different types of paper (table 2).[4] Each paper was cut into one hundred fifty equal-sized small samples for use in Part I of the experiment (immersion treatments) and five larger samples for use in Part II (local treatments).

A few drops of oil were applied to the center of the larger samples, which were placed in drawers on sheets of Mylar to age for a year. The amount of outward spread varied depending on the paper and the oil. The drying and semi-drying oils on the gelatin- and starch-sized papers spread the least. The bacon fat spread outward a bit more, but there was a waxy solid in the center from the crystallization of fat molecules during cooling.

The small samples were dipped into a beaker of oil, dried overnight on blotters, then placed on sheets of Mylar to air dry for up to six weeks before being separated into three groups to undergo three different types of aging. The first set was placed in drawers to be kept in the dark for one year. The second set was strung on linen thread and suspended from the top of a windowsill to be aged at room conditions in direct sunlight for one year. The third set was strung on linen thread and placed into an accelerated aging oven for two weeks.

Table 1. Range of iodine numbers for common oils.

Mineral Oil	0–1
Coconut Oil	8–9.5
Butter	25–40
Beef Tallow & Neat's-Foot Oil	35–50
Palm Oil	53–57
Lard	46–70
Pork Fat	50–75
Olive Oil	79–90
Cottonseed Oil	105–114
Sesame Oil	103–122
Soybean Oil	127–138
Walnut Oil	140–150
Poppy-seed Oil	133–158
Tung Oil	163–171
Cod-liver Oil	145–180
Canola Oil	188–193
Linseed Oil	155–205

Figures obtained from the following sources: Merck index 2001; Gunstone et al. 1994; and Hamilton and Rossell 1986.

Given time restraints, it is sometimes necessary to age samples artificially in order to get preliminary results of research. The natural conditions under which a paper can age are variable, so choosing the best conditions for accelerated aging is also inexact. At normal temperatures, the primary processes occurring during the aging of oils are hydrolysis and oxidation. At higher temperatures, particularly 80°C and above, the evaporation of free fatty acids and other volatile components increases (Erhardt et al. 2000). The artificial aging of other types of oils has not been studied as intensively. The International Organization for Standards, whose members are drawn from paper manufacturers and collection-holding institutions around the world, tests whether papers meet the standards for permanency at the parameters of 80°C and 65% RH (ISO 1994).

Available equipment at the Metropolitan Museum of Art includes an ESPEC Humidity Cabinet LHU–112. At the time of the experiment, the LHU–112 was running at 75°C and 55% RH. As these parameters were acceptable, the samples were aged at that setting. After aging, the chamber-aged set was the most yellow and the dark-aged set was the least. The dark-aged samples were also more likely to retain an oily feel. Comparing the oils, the linseed oil samples were the darkest, followed by sesame oil, olive oil, and bacon fat.

IDENTIFICATION OF OILS

As described above, the color of a stain is a good indication of the relative iodine number. Ultraviolet examination

Table 2. Description of papers used for testing

PAPER	DESCRIPTION	THICK-NESS (mm)	OBSERVABLE PHYSICAL QUALITIES	pH	BIURET TEST FOR GELATIN	IODINE/ POTASSIUM-IODIDE TEST FOR STARCH	PHLORO-GLUCINOL TEST FOR LIGNIN	ALUMINON TEST FOR ALUM	OPTICAL MICRO-SCOPY OF FIBERS
1	Western handmade laid paper of unknown age	.0019	rattles like gelatin-sized paper, smells like gelatin, yellowish in color, opaque	4.5	positive	negative	negative	negative	resembles cotton
2	Strathmore white charcoal paper, recently manufactured, known to be cotton	.0018	slightly textured, optical brighteners	8	negative	positive	negative	negative	resembles cotton
3	Handmade Japanese paper of unknown origin	.0011	soft, off-white, somewhat translucent, long fibers unevenly distributed	4.5	negative	negative	slight positive	negative	*Kozo* fibers with some impurities
4	Whatman #1 filter paper, known to be cotton	.0018	soft, flexible, some texture	5.5	negative	negative	negative	negative	resembles cotton
5	Western wove paper cut from textbook with publication date of 1944	.0009	appearance of discoloration, smooth	4	negative	negative	positive	positive	appears to be wood pulp

or ultraviolet spectroscopy may not be useful for differentiating between different oils. The type of paper and the aging method affected the fluorescence of the samples. Variations in the production of oils can also influence fluorescence (Jamieson 1932).[5]

The microchemical test for unsaturated oils using 1% potassium permanganate reacts with the double bonds in a triglyceride to form the brown precipitate, manganese dioxide (Odegaard et al. 2000).[6] This test works best on oils in liquid form. Nonetheless, it was applied by dropper to some oil-stained paper samples to see if there was any distinguishable difference in the reaction to different dried oils. The drops failed to sink into the stains since the test solution was water-based. As the droplets sat on the surface, they quickly turned brown from exposure to oxygen. A second solution using 50% water and 50% ethanol was also applied by dropper. It sank slowly into all of the samples except those stained with linseed oil, which continued to resist penetration. There was no difference in the reaction on olive oil, sesame oil, and bacon fat samples, suggesting that this method will not distinguish between them.

Gas chromatography/mass spectrometry (GCMS) is a technique that can be used to distinguish different oils although it requires taking a small sample. Raman spec-troscopy is a nondestructive technique that can be employed without taking a sample; however the spectra recorded for some test samples using a 785 nm excitation presented strong fluorescent backgrounds that obscured the signals from the oils. The Fourier transform infrared spectroscopy (FTIR) spectrum for paper has a very large overall signature that obscures the distinguishing peaks for oils.

As part of a joint investigation between the Metropolitan Museum of Art, the Pratt Institute, and New York University on the uses of the NMR mouse (portable, noninvasive, nuclear magnetic resonance) for conservation science research, a team of graduate students working under Silvia Centeno and Eleonora Del Federico has been testing the samples. This technique produces a pulse excitation within a magnetic field to orient the spin of the atoms within a compound, then measures the amount of time necessary for the system to relax to equilibrium. Each compound has a different relaxation curve that depends on such properties as mobility of constituent molecules. Even if this technique is not able to specifically identify an oil, it has potential for providing information about the relative iodine number of a dried oil. The more crosslinked the oil is, the more rigid the polymeric network, and the shorter the time it takes to return to its

original state. The less crosslinked, the freer the molecules are to move, and the longer it takes to return.

PART I: IMMERSION TREATMENTS

The small samples were divided into ten groups, with one sample representing each oil, paper, and aging process in each group. An additional unstained and unaged sample of each paper was added to the groups, bringing the total of each to sixty-five. The experiment consisted of nine immersion treatments and one untreated control (table 3). For each test, the samples were immersed in solutions in individual Petri dishes for a specified period of time with occasional agitation. The following numbered paragraphs explain each treatment:

1. Alkaline water bath
2. Surfactant XL 80–N
   Nonionic surfactant Triton XL–80N was chosen because it is more than 99% biodegradable and low foaming. It is an alcohol alkoxylate (Stavroudis 1995, 10). This product has been discontinued by Dow Chemical but is currently still available from some suppliers. The 1% surfactant solution was found to be pH 4.5 (Stavroudis 2005). The pH was raised to 7 using ammonium hydroxide.
3. Odorless mineral spirits
   Mineral spirits is a nonpolar hydrocarbon solvent obtained from petroleum with a general composition of 81% paraffinic hydrocarbons (straight-chain, unsaturated), 3% naphthenic hydrocarbons, and 16% aromatic hydrocarbons (benzene, toluene, xylene). "Odorless" indicates that the percentage of aromatic hydrocarbons has been reduced. This solvent was chosen for testing because of its low toxicity.
4. Combination of surfactant and high pH
   This treatment tested the theory that the effectiveness of a surfactant could be increased if the stained paper is placed first in a bath with increased pH bath to hydrolyze the triglycerides and then into a surfactant bath to remove them.
5. Enzyme bath
   Lipases catalyze a hydrolysis reaction in triglycerides that breaks them down into component fatty acids and glycerol.[7] Lipase from *candida rugosa* (Sigma #L1754) was used because it is substantially pure and has a high activity for a reasonable price.[8] The optimum temperature is 37°C; however, it was kept at 30°C for this experiment since that is a more reasonable temperature for conservation treatment. The solution was buffered using Trizma Pre-Set Crystals (Sigma #T8068) and the amount was determined using the following concentration calculations (VanDyke 1994):

$$\frac{300 \text{ units of activity/mL} \star 1000 \text{ mL}}{1410 \text{ units of activity/mg}} = .213 \text{ g/ } 1000 \text{ mL}$$

6. Combination of enzyme bath with surfactant
   Treatment 6 was similar to treatment 5, but with the addition of a surfactant to see if this enables the enzymes to work better by breaking the surface tension and giving them better access to the triglyceride molecules.
7. Sodium borohydride
   Sodium borohydride ($NaBH_4$) can lighten the color of oil stains by reducing carbonyl groups to alcohol groups. The high pH of the solution may also cleave some glyceride linkages.
8. Hydrogen peroxide and sodium borohydride
   Hydrogen peroxide lightens the color of paper and stains by oxidizing conjugated double bonds (Timar-Balazsy and Eastop 1998, 225–233).
9. Enzyme bath followed by reducing bleach
   The intention of this treatment is to see if an enzyme bath followed by sodium borohydride is more successful than either treatment alone.
10. Control; no treatment
   This group of samples served as a comparison.

COLORIMETRY

To quantify the changes to the color of the papers, each sample was measured with a colorimeter before and after treatment. This instrument places the color within a three-dimensional graph with the axes of $L\star$ for lightness, $a\star$ for greenness vs. redness, and $b\star$ for blueness vs. yellowness.

Figure 1 shows the average of the change in the $L\star$ value for all of the papers, grouped by oil. An increase in this measurement suggests both lightening and an increase in opacity, since the reading is taken with the sample on a gray background. A change in the $L\star$ value of less than five was a barely detectable visual difference, while a change in the $L\star$ value of ten or more was significant. Treatment 9 was the best overall method of stain reduction, but even with this treatment the overall color change for the linseed oil samples was in the barely detectable range. Olive oil and bacon fat samples lightened the most in all of the baths, as expected because they are the most saturated, followed by sesame oil. Figure 2 shows the same results broken down by paper. The only average $L\star$ value that decreased was that for the linseed oil on gelatin paper samples. The stains on the starch-sized and alum-sized papers became the lightest.

Figure 3 shows the change in the average $b\star$ value, or yellowness, for all of the papers, which would be expected to decrease after treatment. In fact, linseed oil samples increased in yellowness in every group except treatment 9. Interestingly, those from treatments 5 and 6 (lipase with and without surfactant) yellowed more than the untreated control group. It is likely that this increase was not caused by the treatments, but rather due to continued crosslinking and oxidation in the period of time between the colorimetry measurements. Figure 4 breaks the $b\star$ value results

Table 3. Immersion treatments

	IMMERSION TREATMENTS	PROCEDURE	OBSERVATIONS AND RESULTS*
T1	Alkalized baths (pH 8.5) 30°C	Step 1: Humidified overall for 35 minutes Step 2: Immersed in deionized water raised to pH 8.5 with ammonium hydroxide and heated to about 30°C for 1 hour Step 3: Immersed in deionized water raised to pH 8.5 with ammonium hydroxide and heated to about 30°C for 1 hour Step 4: Rinsed in deionized water raised to pH 7 with ammonium hydroxide for 1 hour Step 5: Air dried	This treatment was the least successful. The majority of the samples remained oily in appearance and feel, with some moderate reduction on the paper 1 samples and the olive oil samples.
T2	Non-ionic surfactant XL 80-N 23°C	Step 1: Humidified overall for 45 minutes Step 2: Immersed in deionized water with 1% Triton XL 80-N for 1 hour Step 3: Rinsed in deionized water raised to pH 7.5 with ammonium hydroxide for 1 hour Step 4: Rinsed in deionized water raised to pH 7.5 with ammonium hydroxide for 1 hour Step 5: Air dried	Only treatment 3 was less damaging to the surface of the papers than this one, but overall the majority of the samples were still oily in appearance and feel after treatment. The samples continue to emit the scent of the surfactant two years later, indicating that residues remain.
T3	Mineral spirits 23°C	Step 1: Immersed in mineral spirits for 1.5 hours Step 2: Air dried	This treatment was the least damaging to the surface of the papers. For samples aged in the window or chamber, this was generally not a successful treatment; however it worked well on the olive oil, bacon fat, and sesame oil dark-aged samples. Generally, the stains remained darkest in the last area of the paper from which the solvent evaporated, indicating that the oils were somewhat mobile in the solvent.
T4	Non-ionic surfactant XL 80-N at pH 8.5 23°C	Step 1: Humidified 45 minutes Step 2: Immersed in bath with 1% Triton XL 80-N raised to pH 8.5 with ammonium hydroxide Step 4: Rinsed in deionized water raised to pH 7.5 with ammonium hydroxide Step 5: Rinsed in deionized water raised to pH 7.5 with ammonium hydroxide Step 6: Air dried	In a direct comparison with treatment 2, the effectiveness of the surfactant was generally increased when the pH was raised (for 80% of the samples). The lingering scent of surfactant calls into question whether this is a worthwhile treatment to pursue.
T5	Lipase enzyme bath 30°C	Step 1: Humidified 45 minutes Step 2: Immersed in deionized water with lipase at 30°C and raised to ~pH 7.5 with Trizma Pre-set Crystals for 1 hour Step 3: Immersed in deionized water raised to ~pH 7.5 with Trizma Step 4: Air dried and evaluated Step 5: Placed in bath of lipase in deionized water at 30°C and pH ~7.5 for 3 hours Step 6: Immersed in deionized water raised to pH 7.5 with Trizma Step 7: Air dried	Paper 5 samples (alum-rosin) became a cold yellow tone after enzyme treatment. This treatment was successful in reducing the oily feel and appearance of a large number of the samples (59.5%), with a softening that indicated some loss of sizing in 17% of the samples.
T6	Combination enzyme bath with surfactant 30°C	Step 1: Humidified for 45 minutes Step 2: Immersed in deionized water Step 3: Immersed in deionized water at pH 7.7 with lipase and 1% Triton XL 80-N for 1 hour Step 4: Immersed in deionized water at pH 7.7 with lipase and 1% Triton XL 80-N for 3 hours Step 5: Immersed in deionized water raised to pH 7.7 with Trizma for 1 hour Step 6: Air dried	The oil was reduced from 74.7% of the samples, according to feel and appearance. Some samples (11.7%) became soft and limp, indicating a loss of sizing or strength; 8.5% of the samples were lighter than the unstained and untreated control after treatment (i.e., over-lightened). All of these were from the bacon fat set, either paper 3 or paper 5. In comparison to treatment 5, 83.3% of the samples were lighter after treatment 6, suggesting that adding the surfactant to the enzyme did improve the performance of the enzyme; 6.8% were equally lightened by both treatments, while 11.7% were lighter after treatment 5, all from the dark-aged set.

Continued on next page

*Percentages are calculated out of 60 samples in each group

Table 3 *(cont.)*. Immersion treatments

	IMMERSION TREATMENTS	PROCEDURE	OBSERVATIONS AND RESULTS*
T7	Sodium borohydride (reducing bleach) 23°C	Step 1: Humidified for 45 minutes Step 2: Immersed in deionized water raised to pH 8.5 with ammonium hydroxide for 1 hour Step 3: Immersed in .2% sodium borohydride in deionized water for 35 minutes (after allowing gas to evolve for 30 minutes) Step 4: Rinsed in deionized water Step 5: Rinsed in deionized water raised to pH 8.5 with calcium hydroxide for 1 hour Step 6: Air dried	This treatment reduced the oily appearance of 34% of the samples, but it was very damaging to the surface of the papers, especially with lower iodine number oils. The surface was damaged to an unacceptable degree for 20.4% of the samples. Some of the samples (17.6%) were over-lightened. After treatment 8.5% of the samples were very soft and limp, suggesting a loss of sizing or strength. It turned paper 5 (alum-rosin) to a somewhat grayer color than those not treated with bleach.
T8	Hydrogen peroxide and sodium borohydride (oxidizing then reducing bleach) 23°C	Step 1: Humidified Step 2: Immersed in deionized water raised to pH 7.5–8 using calcium hydroxide Step 3: Immersed in 3% hydrogen peroxide solution raised to pH 8.5 using calcium hydroxide Step 4: Rinsed in deionized water bath Step 5: Immersed in deionized water raised to pH 7.5–8 using calcium hydroxide Step 6: Immersed in deionized water raised to pH 7.5–8 using calcium hydroxide Step 7: Air dried Step 8: Humidified for 45 minutes Step 9: Immersed in .2% sodium borohydride in deionized water for 35 minutes (after allowing gas to evolve for 30 minutes) Step 10: Rinsed in deionized water Step 11: Rinsed in deionized water raised to pH 8.5 with calcium hydroxide for 1 hour Step 12: Air dried	Overall, this treatment was more successful than treatment 7. As in treatment 7, it did not work as well on the chamber-aged samples: there was surface-damage of the papers, and paper 5 (alum-rosin) became grayer. After treatment, 61.2% of the samples were judged to be noticeably reduced of oil, but 28.9% samples had visible damage or alteration of the surface texture. Half of the linseed oil samples were still just as dark after treatment as the samples that had not been treated at all. The linseed oil samples were the least likely to be damaged. This treatment may be too harsh and unnecessary for less crosslinked stains, and it might be inadequate for more crosslinked stains. It is best for semi-drying oils.
T9	Enzyme bath followed by reducing bleach 23°C	Step 1: Humidified for 45 minutes Step 2: lipase bath in deionized water at pH 7.7 and 1% Triton XL 80-N for 1 hour Step 3: Immersed in bath of lipase in deionized water with 1% Triton XL 80-N, raised to pH 7.7 with Trizma, for 3 hours Step 4: Immersed in deionized water raised to pH 7.7 with Trizma for 1 hour Step 5: Air dried Step 6: Humidified for 45 minutes Step 7: Immersed in deionized water raised to pH 8.5 with ammonium hydroxide for 1 hour Step 8: Immersed in .2% sodium borohydride in deionized water for 35 minutes Step 9: Rinsed in deionized water Step 10: Rinsed in deionized water raised to pH 8.5 with calcium hydroxide for 1 hour Step 11: Air dried	The results for this treatment were the best overall, but it was too harsh for the bacon fat and olive oil stains. A large proportion (43.5%) of the samples were over-treated: 16.7% from the bacon fat set, 15% from the olive oil set, and 10% from the sesame oil set. One sample from the linseed oil set (paper 1, dark- aged) showed surface damage, while the oil stain was not adequately reduced. The darkest samples after treatment were from the papers 1, 2, and 5 linseed oil sets. In comparison with treatment 6: 73.5% of the samples were lighter after treatment 9, 22% were lighter after treatment 6, and 5% were not effectively lightened with either treatment, all from the linseed oil set. In comparison with treatment 8: 67% of the samples were lighter after treatment 9; 27% of the samples were lighter after treatment 8; and the same 5% were not effectively lightened with either treatment. Among those lightened more by treatment 8 were all of the chamber-aged olive oil samples on gelatin-sized and alum-sized papers.
T10	Control—no treatment		

*Percentages are calculated out of 60 samples in each group

down by paper to show that the greatest amounts of yellowing occurred with the Whatman filter paper, the gelatin-sized paper, and the Japanese paper.

VISUAL EXAMINATION

Colorimetry does not take into account any damage to the samples caused by the treatments. For bacon fat and olive oil in particular, treatments 3, 5, or 6 were adequate to lighten the samples, while those involving bleaches were too harsh. Visual examination was also conducted on each sample. In all, 106 samples were found to be damaged in some way, out of six hundred total. Figure 5 shows the number of samples of each paper that were damaged, out of 120 each. Figure 6 shows the number of samples of each oil that were damaged, out of 150 each. Figure 7 shows the number of samples damaged for each treatment, out of sixty each. The light gray bars reflect the number of samples with damage in each category, while the dark gray bars represent the degree of damage. This second amount was obtained by giving the damage a score of one to three points, assigning one point when the paper was over-lightened or slightly limp, two points for both of the above or when the paper was noticeably weakened, and three points when the treatment caused blistering of the paper surface.

PART II: LOCAL TREATMENTS

Frequently, the medium of an artwork or artifact will preclude immersion treatment. For this reason, it is often necessary to perform local treatments.

As Part II of this research, local methods of treatment were tested on the larger samples.[9] Each of the stains were divided into squares of roughly one centimeter using a pencil and local tests were carried out in each square. See table 4 for a list of every local treatment attempted along with observations and results. In general, the stains on the gelatin-sized paper were the hardest to reduce, followed by the starch-sized, the alum-rosin sized, the Japanese paper, and the Whatman paper.

Since the enzyme baths worked very well on oils with a lower iodine number, three types of poultices were mixed with lipase for testing: agarose, 5% methyl cellulose A4M,
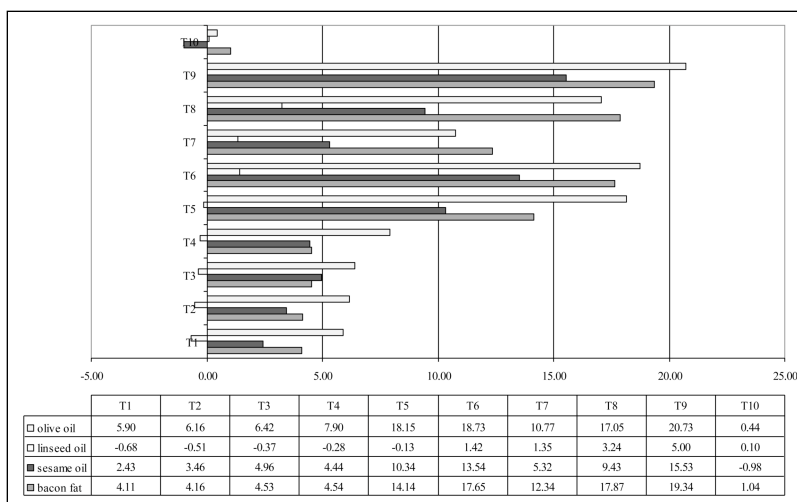

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
olive oil	5.90	6.16	6.42	7.90	18.15	18.73	10.77	17.05	20.73	0.44
linseed oil	-0.68	-0.51	-0.37	-0.28	-0.13	1.42	1.35	3.24	5.00	0.10
sesame oil	2.43	3.46	4.96	4.44	10.34	13.54	5.32	9.43	15.53	-0.98
bacon fat	4.11	4.16	4.53	4.54	14.14	17.65	12.34	17.87	19.34	1.04

Fig. 1. Average change in L★ for all treatments

	Change in L* paper 1	Change in L* paper 2	Change in L* paper 3	Change in L* paper 4	Change in L* paper 5
olive oil	15.58	8.07	8.00	8.55	14.85
linseed oil	0.65	-1.79	2.63	2.65	0.43
sesame oil	7.84	5.45	5.36	6.99	8.60
bacon fat	11.83	7.86	8.96	7.76	13.46
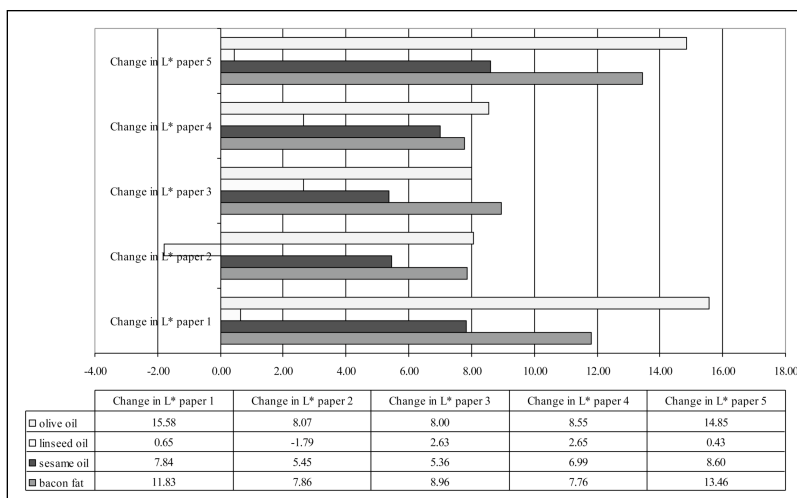
Fig. 2. Average change in L★ after treatment by paper

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
olive oil	-0.83	-1.20	0.74	-0.86	-2.95	-4.22	-3.17	-5.65	-5.74	1.55
linseed oil	2.56	3.30	3.01	3.86	5.33	4.91	2.24	0.50	-1.24	3.95
sesame oil	0.50	0.24	1.58	-0.14	0.10	-3.03	-0.70	-3.17	-4.67	1.92
bacon fat	-0.88	-0.94	0.49	-0.15	-1.18	-3.03	-3.04	-4.90	-5.06	-0.06
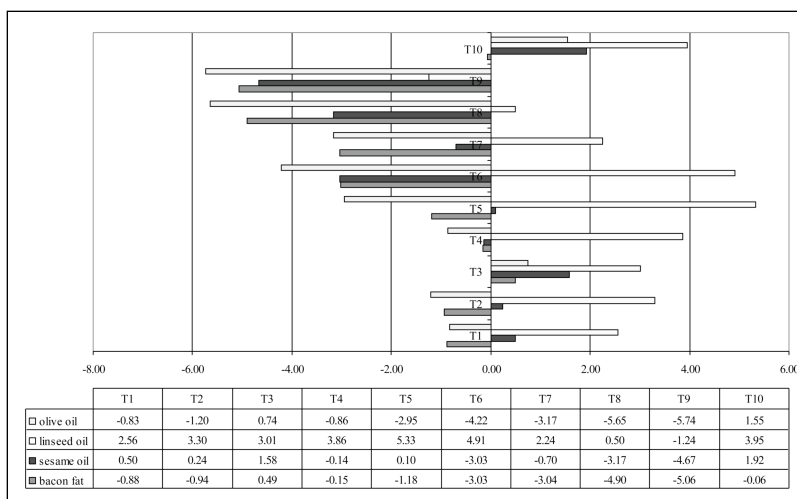
Fig. 3. Average change in b★ for all treatments

	Change in b* paper 1	Change in b* paper 2	Change in b* paper 3	Change in b* paper 4	Change in b* paper 5
☐ olive oil	-2.94	-3.20	-2.47	-1.10	-3.54
☐ linseed oil	0.90	4.10	3.07	5.05	0.99
■ sesame oil	-0.50	-1.61	-0.93	-0.74	-1.39
■ bacon fat	-3.72	-2.17	-1.43	-0.20	-2.88
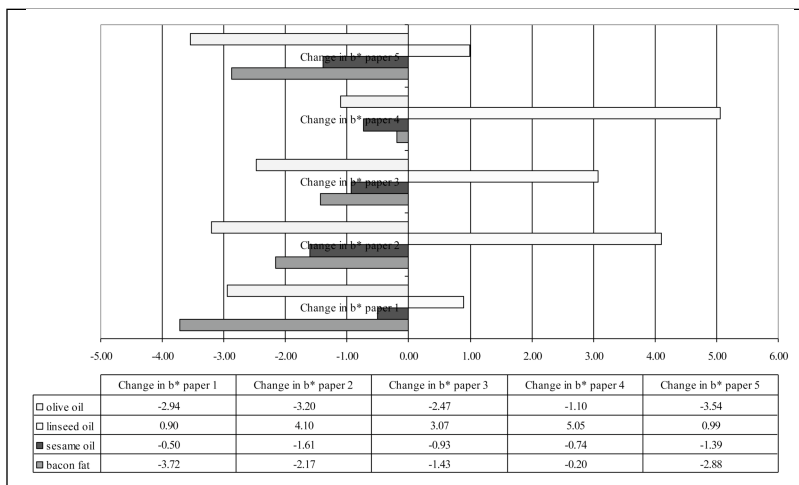
Fig. 4. Average change in b★ after treatment by paper

	Paper 1	Paper 2	Paper 3	Paper 4	Paper 5
☐ Total Samples with Damage	29	10	42	2	23
■ Degree of Damage	68	16	53	2	61
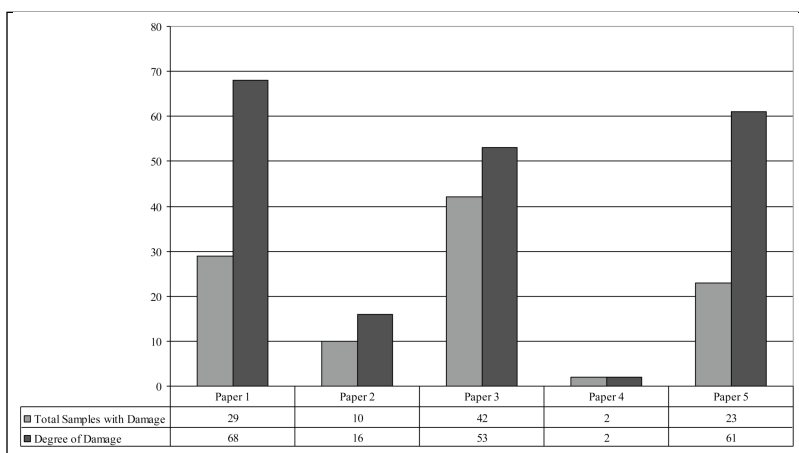
Fig. 5. Samples damaged during treatment (by paper)

	Bacon fat	Olive oil	Sesame oil	Linseed oil
☐ Total Samples with Damage	43	38	24	1
■ Degree of Damage	82	71	44	3
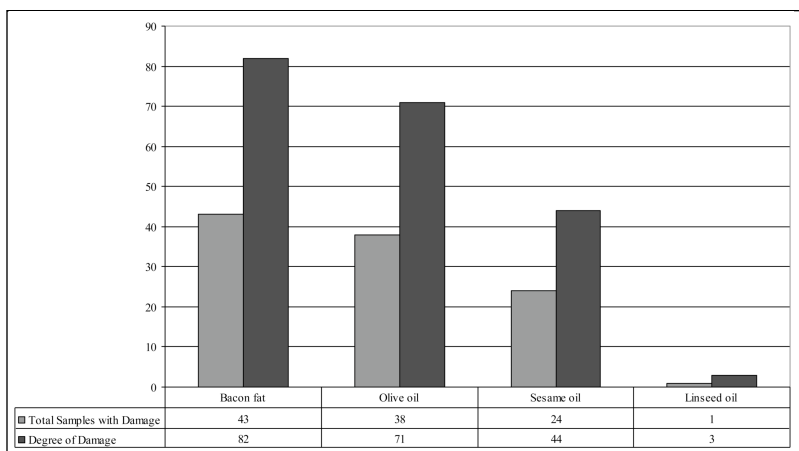
Fig. 6. Samples damaged during treatment (by oil)

and laponite. The methyl cellulose and laponite were already prepared. A small amount of each was mixed with less than 0.01 g of lipase. Three different agarose gels were prepared: one with surfactant only, one with surfactant and lipase, and one with lipase only. To prepare the agarose, 25 mL of water was mixed with 0.3 g of powdered agarose and added to 0.003 g of lipase and/or .25 mL of Triton XL–80N. The agarose, surfactant, and water were heated to just under 100°C. The enzyme was added as the mixture cooled, just before pouring it into a Petri dish to set (van Dyke 1994, 102). After setting, the agarose was cut into cubes.

The agarose poultices containing lipase were very successful in reducing the nondrying and semi-drying oils, but it was difficult to control the area of application. There was a lateral spread of moisture away from the agarose poultices with yellow tidelines at the edge of the moist area. Methyl cellulose and laponite were more likely to leave behind residues and required more mechanical action to remove, so the surface texture of the paper was more likely to be disrupted. A piece of *gampi* paper used as a barrier between the poultice and the stain eliminated these problems, but also resulted in less stain reduction (Warda et al. 2007).

Since mineral spirits reduced some of the stains without affecting the surface texture in Part 1, toluene was included in the local tests. Toluene was extremely effective on olive oil and bacon fat, but the lateral spread was difficult to control, even over suction. It lightened the alum-rosin paper in the treated spot more than the rest of the sheet, perhaps because sizing or discoloration was flushed out as well. For olive oil stains, one drop of toluene was enough to reduce the stain completely within the square. Multiple drops were necessary for complete reduction of the bacon fat stains within the squares. On every paper except the gelatin-sized, the fatty deposits in the center were also reduced. On the sesame oil stains, the results were mixed, with the best results on the Whatman filter paper and the most disappointing on the starch-sized paper. For sesame oil, multiple applications of toluene were necessary, and there were still oil residues left in the cavities of textured papers.

Generally, the linseed oil stains could not be completely reduced. Lipase-agarose poultices followed with sodium borohydride were the

most effective. Hydrogen peroxide followed by sodium borohydride was also effective. These results were similar to those from Part I.

Because the results on the linseed oil samples were disappointing, further testing was done on several drawings in a variety of media from the author's sketchbook that were accidentally stained with linseed oil over fifteen years ago. The sketchbook paper was Strathmore wove, wood-pulp paper with starch sizing.

Solvent testing was limited in Part I because of the large sample population. But the promising results with mineral spirits and toluene on the nondrying and semi-drying oils suggested that it was necessary to do some follow-up tests on linseed oils using a wider range of solvents. For the initial tests, the following solvents were applied by dropper over suction six times: toluene, methanol, pyridine, tetrahydrofuran (THF), and methyl ethyl ketone (MEK). THF was found to be the best solvent, followed by pyridine and methanol, but two or more solvents in succession appeared to remove different components of the stain and were more effective than any single solvent alone.

Further testing indicated that the amount of solvent used is not as important as the amount of time the solvent is kept in contact with the stain. Many techniques for holding the solvent against the oil were tried, such as saturating a blotter with solvent and covering it with glass, or saturating poultices with solvent. The best method for preventing evaporation and lateral spread was to put the solvent in a well made of fuller's earth and covered with glass. After the solvent has completely evaporated and the fuller's earth is brushed away, more of the oil can be flushed out over suction while applying the solvent by dropper.

Solvent treatment does not reduce drying oil stains completely, however. Most likely, the solvents are removing free fatty acids, oxidation byproducts, and other unbound components, but are unable to break up the network structure. Combinations of agarose-lipase poultices and bleaching both before and after solvent treatment were tried. Better results were obtained when nonaqueous solvents were applied before aqueous ones. Water swells the fibers, altering the paper texture and possibly causing the stain to become even more entrenched.

CONCLUSIONS AND RECOMMENDATIONS

The oils on chamber-aged and light-aged samples were darker and more difficult to treat than those that were dark-aged. Of the papers used in this experiment, the most sensitive to treatment were the starch-sized paper, the Japanese paper, and the alum-rosin paper. The alum-rosin paper was over-lightened by solvent treatment. This suggests that the composition of the paper should be considered before treatment in terms of the potential risk to the paper. Of the oils used in this experiment, those with high iodine numbers were more difficult to treat than those with low iodine numbers. Generally, the darkness and yellowness of the oil stains are more intense the higher the iodine number of the oil.

Lighter stains are likely to come from oils with a lower iodine number, so milder treatments are required. Dark stains are likely to be a drying oil. It may not be possible to reduce drying oil stains completely; however, drying oil stains provide some protection to the paper during treatment, so the area may be able to withstand multiple campaigns of treatment. It is better to use nonaqueous solvents before aqueous ones. Nonaqueous treatment causes less disruption of the paper surface than aqueous treatment.

Lipase-agarose poultices reduced more discoloration than lipase-laponite or lipase-methyl cellulose poultices with less surface damage, but there was some lateral spread of moisture and tidelines. Although surfactants were tested, they are not recommended due to the lingering odor from immersion treatments and the increased lateral spread during local treatments.

If the stain is pale in color, it may be possible to reduce it adequately with mineral spirits, toluene, a lipase-agarose poultice, and/or sodium borohydride. Darker stains are likely to be very oxidized, so complete reduction may not be possible. THF, methanol, pyridine, a lipase-agarose poultice, and/or hydrogen peroxide followed by sodium borohydride were successful in flushing some discoloration from the linseed oil stains.

FUTURE RESEARCH

To further understand the long-term results of each treatment, colorimetry will be performed again on the samples in a few years to
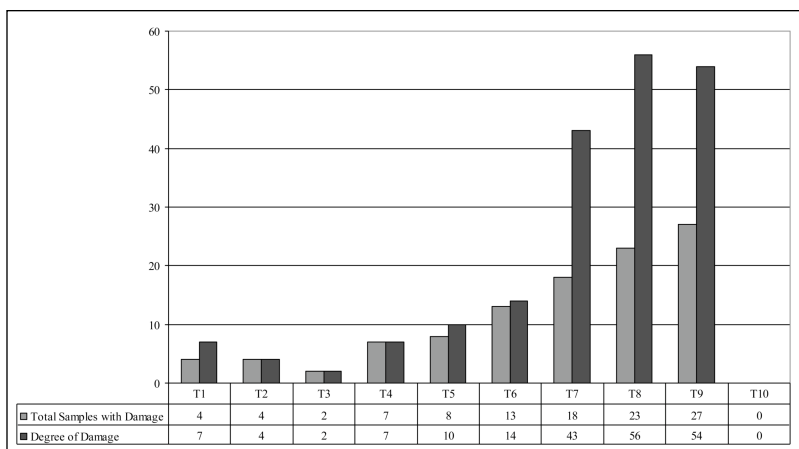

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Total Samples with Damage	4	4	2	7	8	13	18	23	27	0
Degree of Damage	7	4	2	7	10	14	43	56	54	0

Fig. 7. Samples damaged during treatment (by treatment)

Table 4. Local treatments, listed from least effective to most effective

	LOCAL TREATMENT	PROCEDURE*	OBSERVATIONS AND RESULTS
T1	Deionized water	Deionized water brought to pH 8.5 with NH₄OH: applied by dropper over suction.	Not very successful.
T2	Lipase in water	Solution of lipase in deionized water buffered to pH 7.7 with Trizma: kept warm and brushed onto the stain surface; allowed to sit on the surface for about 10 minutes, then rinsed over suction.	Not very successful.
T3	Lipase in laponite over *gampi*	7.5% laponite mixed with .01 g of lipase over *gampi* barrier paper: allowed to sit 1 hour, then removed and rinsed.	*Gampi* barrier paper prevented residues and disruption of paper surface, but the stains were not reduced as well as they were without the barrier.
T4	Lipase in methyl cellulose over *gampi*	5% methylcellulose A4M mixed with .01g of lipase: applied to the stain over a barrier of *gampi* Japanese tissue and allowed to sit for 1 hour then rinsed.	*Gampi* barrier paper prevented residues and disruption of paper surface, but the stains were not reduced as well as they were without the barrier.
T5	Mineral spirits	Mineral spirits allowed to sit on the surface for 10 minutes, then pulled through the paper over suction.	The mineral spirits evaporated very slowly from the stains. Evaporation was particularly slow with paper 1, the gelatin-sized paper. This treatment worked well for olive oil on the starch-sized and Japanese papers, for bacon fat on every paper except the gelatin-sized paper, and for sesame oil on the alum-rosin paper. It did not work on any of the linseed oil samples.
T6	Lipase in laponite	7.5% laponite mixed with .01g of lipase: sat directly on the stain for one hour before it was scraped off and rinsed.	Some residues and disruption of paper surface were evident after treatment.
T7	Lipase in methyl cellulose	5% methylcellulose A4M mixed with .01g of lipase: sat directly on the stain for one hour before it was scraped off and rinsed.	Shiny residues were left behind due to incomplete removal when scraping it off before rinsing. The most residues were left behind by the methylcellulose, followed by laponite, then agarose. This technique also resulted in the greatest disruption of the paper surface.
T8	Lipase in agarose over *gampi*	Poultice of lipase in agarose over *gampi* Japanese tissue: removed after 10 minutes and rinsed.	*Gampi* barrier paper did help to alleviate tidelines, lateral wicking of moisture, and residues. The effectiveness was lowered, but this may be a good option in places were the stain is close to the media and the lateral spread needs to be controlled.
T9	Lipase and surfactant over *gampi*	Poultice of lipase and surfactant in agarose over *gampi* Japanese tissue: removed after 10 minutes and rinsed.	Same as above.
T10	Surfactant in agarose	Poultice of surfactant in agarose: removed after 10 minutes and the area was rinsed over suction.	The moisture from the agarose spread laterally very quickly with a yellow tideline at the outer edge of the moisture, especially when there was surfactant added. This suggests that it would be difficult to confine this treatment to a controlled area. The spread occurred fastest on Whatman filter paper, followed by the Japanese paper, the Strathmore paper, the alum-rosin paper, and the gelatin paper. The lateral spread occurred fastest on the linseed oil, followed by bacon fat, sesame oil, and olive oil. The tidelines could be reduced over suction with alkaline water. In some cases the paper buckled from the moisture in the gel. Buckling happened most often with paper 2, the modern Strathmore paper, and least often with paper 1, the gelatin-sized paper. To limit tidelines and buckling, the poultice time was limited to 10 minutes.
T11	Surfactant and lipase in agarose	Poultice of surfactant and lipase in agarose: removed after 10 minutes and rinsed.	As above, there was lateral spread and tidelines.
T12	Lipase in agarose	Poultice of lipase in agarose: removed after 10 minutes and rinsed.	With lipase only in agarose, there was still lateral spread and tidelines, but not as much as the gels with surfactant added.
T13	Toluene	Toluene: applied 6 times by dropper over suction.	This was the best treatment for every stain except for the linseed oil stains. It resulted in the best stain reduction and the least surface disruption.

*Rinsing was with deionized water brought to pH 8.5 with ammonium hydroxide, unless stated otherwise.

Table 4 *(cont.)*. Local treatments, listed from least effective to most effective

	LOCAL TREATMENT	PROCEDURE*	OBSERVATIONS AND RESULTS
T14	Hydrogen peroxide	3% hydrogen peroxide: applied, allowed to sit 20 minutes, rinsed, then followed with 0.2% sodium borohydride, then rinsed again (linseed oil only).	This treatment also worked quite well for all of the samples.
T15	Lipase in agarose, then sodium borohydride	Poultice of lipase in agarose: rinsed after 10 minutes, then dried; 0.2% sodium borohydride was brushed onto the surface repeatedly for 20 minutes, then the area was rinsed again (linseed oil stains only).	The poultice alone was not adequate for reduction of linseed oil, so it was followed with a bleaching step. This treatment was the second-best treatment for the linseed oil stains.
T16	Surfactant and lipase in agarose, then sodium borohydride	Poultice of surfactant and lipase in agarose: rinsed after 10 minutes, then dried; 0.2% sodium borohydride was brushed onto the surface repeatedly for 20 minutes, then the area was rinsed again (linseed oil stains only).	This treatment was the best one for all of the linseed oil samples.

*Rinsing was with deionized water brought to pH 8.5 with ammonium hydroxide, unless stated otherwise.

see if the color has changed significantly in that time. As mentioned above, the aged and treated samples are being tested using in situ NMR. The findings from this research may be topics for future discussions or articles.

NOTES

1. Expression is the process often used with edible oils, while solvent extraction, which is cheaper and easier, is used for industrial oils.

2. Iodine number ranges vary depending on the source.

3. Initially, the experiment included mineral oil, which is obtained from petroleum and has an iodine number of 0–1. The mineral oil samples were eliminated because (1) the sample population was too large; (2) in most cases, the mineral oil samples were not darker than the set left unstained; and (3) the mineral oil appeared to react with the plastic slide pages in which they were stored after aging, potentially tainting the samples. All of the oils were commercially packaged except for the animal oil, which was obtained by melting and filtering bacon fat leftover from cooking.

4. Microchemical tests and fiber microscopy were conducted to determine fiber type and sizing of potential candidates.

5. According to Jamieson, refined olive oil gives a blue fluorescence, while virgin olive oil fluoresces yellow or yellowish-brown. Sometimes yellow pigment is added to a refined oil to give it a yellow fluorescence. Linseed oil can be bleached by filtering it through fuller's earth while hot.

6. There is another microchemical test for triglycerides available from Sigma called GPO-Trinder Reagent. It was not tested on these samples due to its severe health rating.

7. See Blüher et al. 1997, Grabauskaite et al., Larminie 1992, Makes 1990, and Wolbers 2000 for other descriptions of the use of lipase enzymes to reduce oil stains.

8. Wolbers (2000) describes using Sigma Type VII lipase, *candida cylindracea,* in gel form to remove a linseed oil layer from paintings. Blüher et al. used four different lipases: the *candida cylindracea* mentioned above; porcine pancreas 6%, Sigma Type II; lipolase 30T 5% and Lipomax (Novo) 5%. The *candida cylindracea* was tested both as a gel and as an immersion treatment. The other lipases were tested only as immersion treatments. Larminie used Sigma Type VII and Type VII-S. She found the Type VII to be the best option because Type VII-S is highly active and it is difficult to measure out the small amounts needed. She also found that the Type VII worked adequately at room temperature, although 37°C is ideal for optimum performance. Grabauskaite et al. tested *Ps. mendocina,* purified at Vilnius University's Biochemistry and Biophysics Department.

9. The sample with olive oil on Whatman filter paper was not tested because the oil spread evenly to every edge of the paper and did not create any discernable discoloration.

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