

NMR Studies of Pigment Sunscreen Interactions

A new type of hydrophobic surface treatment for sunscreen pigments produces lipophilic dispersion properties, and simultaneously mitigates unwanted chromophore side-reactions between organic UV absorbers and Fe compounds. This surprising benefit can facilitate the formulation of new families of sunscreen products that contain both iron-based pigments and organic UV absorbers (U.S. Patent 7,387,795).

n-octylphosphonic acid (NOPA)

vs.

n-octylsilane (NOS)

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Portions of this presentation were given at The University of Akron NMR Users Meeting (Akron, OH November 2009); and at the 6th International Symposium on Silanes and Other Coupling Agents (Cincinnati, OH June 2007).

BACKGROUND CONCEPTS

Hydrophobic Coatings for Inorganic Powders

Hydrophobic / Lipophilic inorganic powders are desirable for use in certain cosmetics formulations.

Powders are surface treated to facilitate the selective dispersion of particles in the oil-phase of either oil-in-water or water-in-oil based systems (i.e. sunscreen formulations that contain particulates of TiO_2 and/or ZnO).

Alkyltrialkoxysilanes such as n-octyltriethoxysilane (NOS) are used extensively in these types of applications. Alkylphosphonic acids such as n-octylphosphonic acid (NOPA) are possible alternatives (U. S. Patent 7,387,795).



Alkyltrialkoxysilanes vs. Alkylphosphonic Acids

Further Background Reading:

Parker, A. A., et al., "Comparative Studies of Hydrophobic Surface Treatments for TiO₂: n-Octylphosphonic Acid and n-Octyltriethoxy silane," in Silanes and Other Coupling Agents, Volume 4, K.L. Mittal, Editor, VSP BV, The Netherlands, 2007 pp. 399-409.

Parker, A. A., Wagler, T., "Solid State NMR Studies of a Hydrophobic Surface Treatment for TiO₂: n-Octylphosphonic Acid," in Silanes and Other Coupling Agents, Volume 5, K.L. Mittal (Ed.), VSP/Brill, Leiden, The Netherlands, 2009 pp. 323-331.

"Cosmetic Compositions Containing Organophosphonic Acid Coated Particulates and Methods of Producing the Same," U. S. Patent 7,387,795, June 17, 2008.

What are the similarities and differences between NOS and NOPA?

This presentation will focus on three comparative phenomena with each being related to the end-use application (i.e., sunscreen formulation & performance):

- ***Yellow iron oxide & avobenzene degradation***
- ***TiO₂ dispersions in water & in oil***
- ***Self-assembled monolayer (SAM) formation***

Hydrophobic surface treatments enable these surface-treated iron oxide pigments to float on water.



NOS vs. NOPA

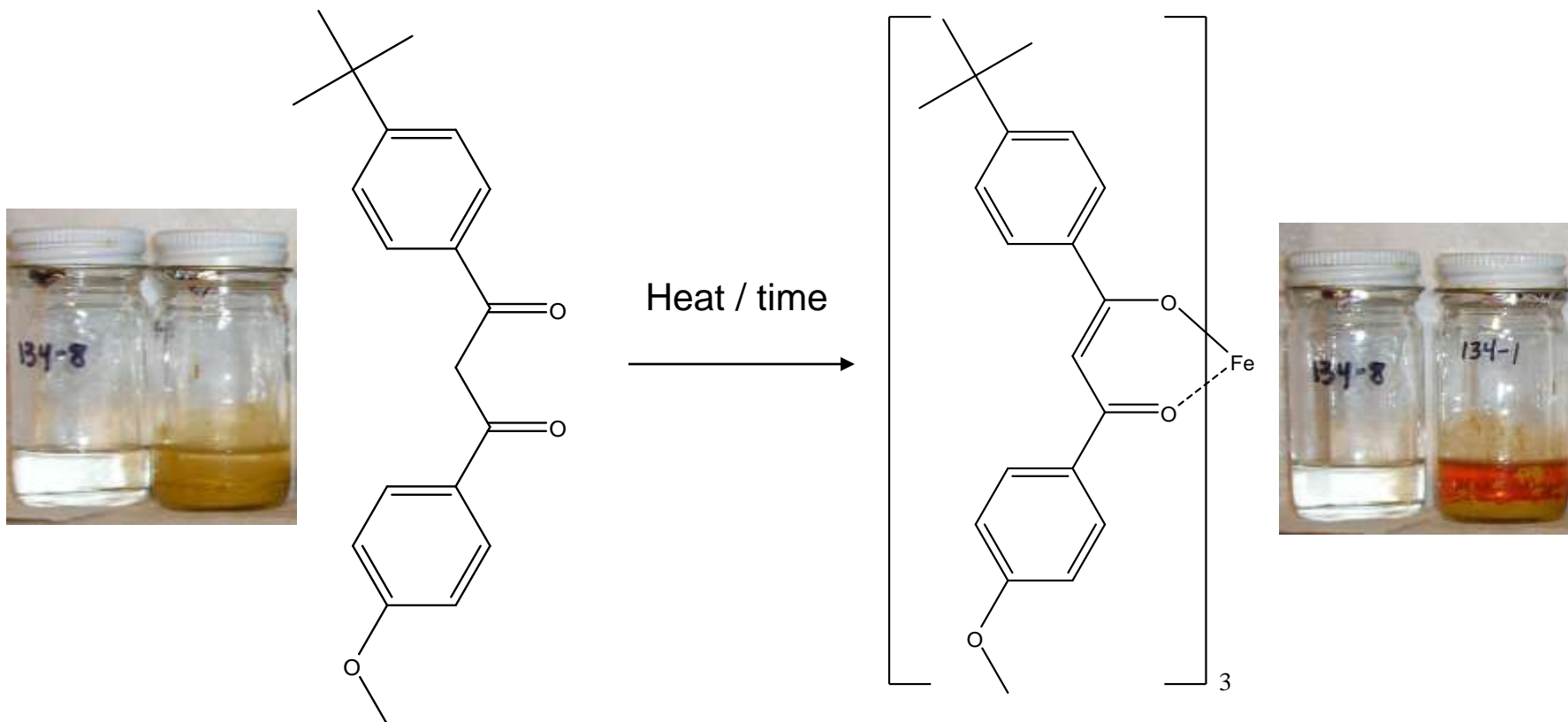
Yellow iron oxide &
avobenzone degradation



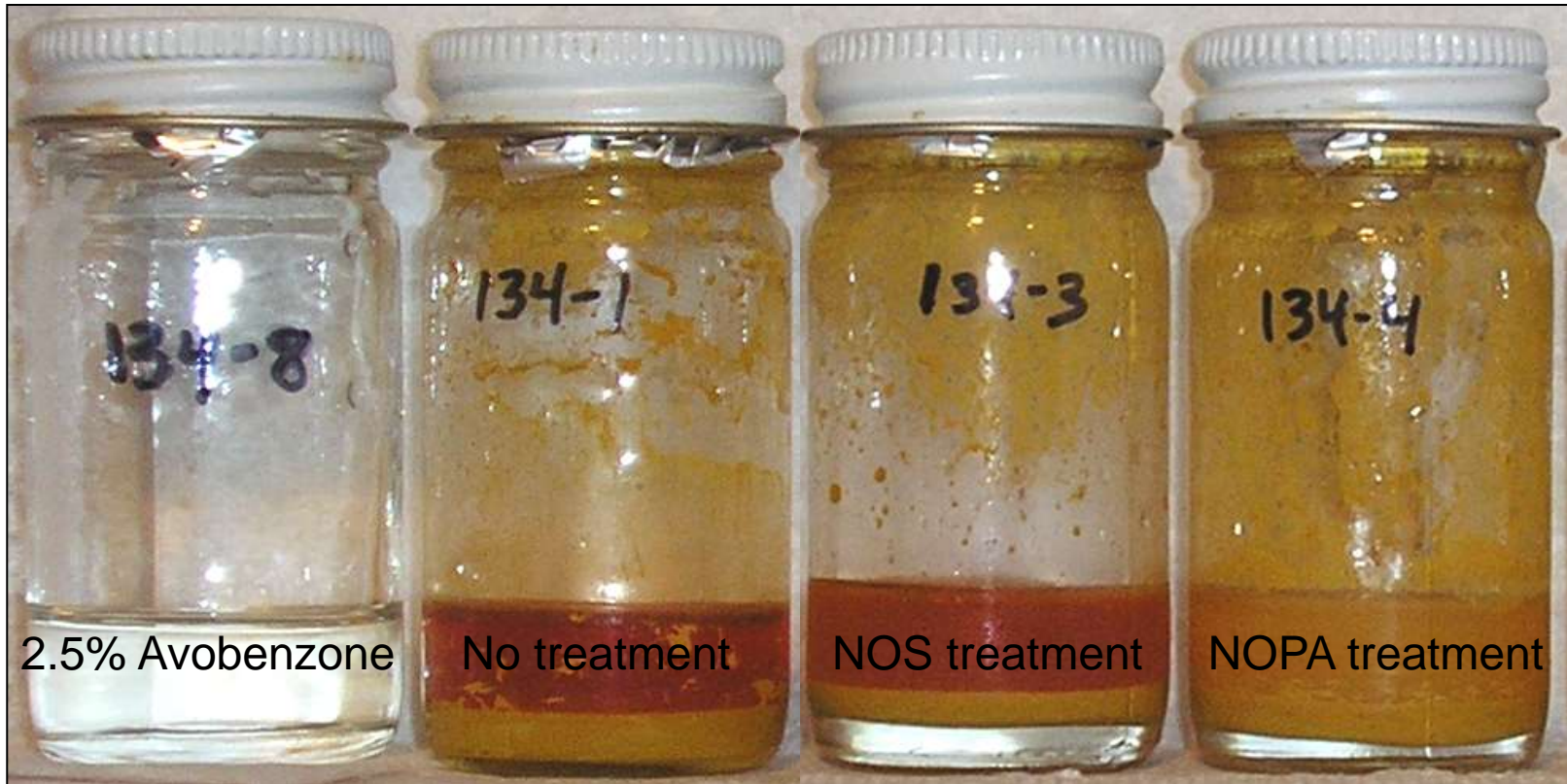
Inorganic Pigments with Sunscreens – Side Reactions

Organic UV absorbers such as avobenzone are often used in sunscreens.

When certain inorganic pigments are added to these types of sunscreen formulations, unwanted side reactions can occur. For example, yellow iron oxide (Fe_2O_3 hydrate) will cause the carrier liquid (caprylic triglyceride) to turn orange in the presence of avobenzone.



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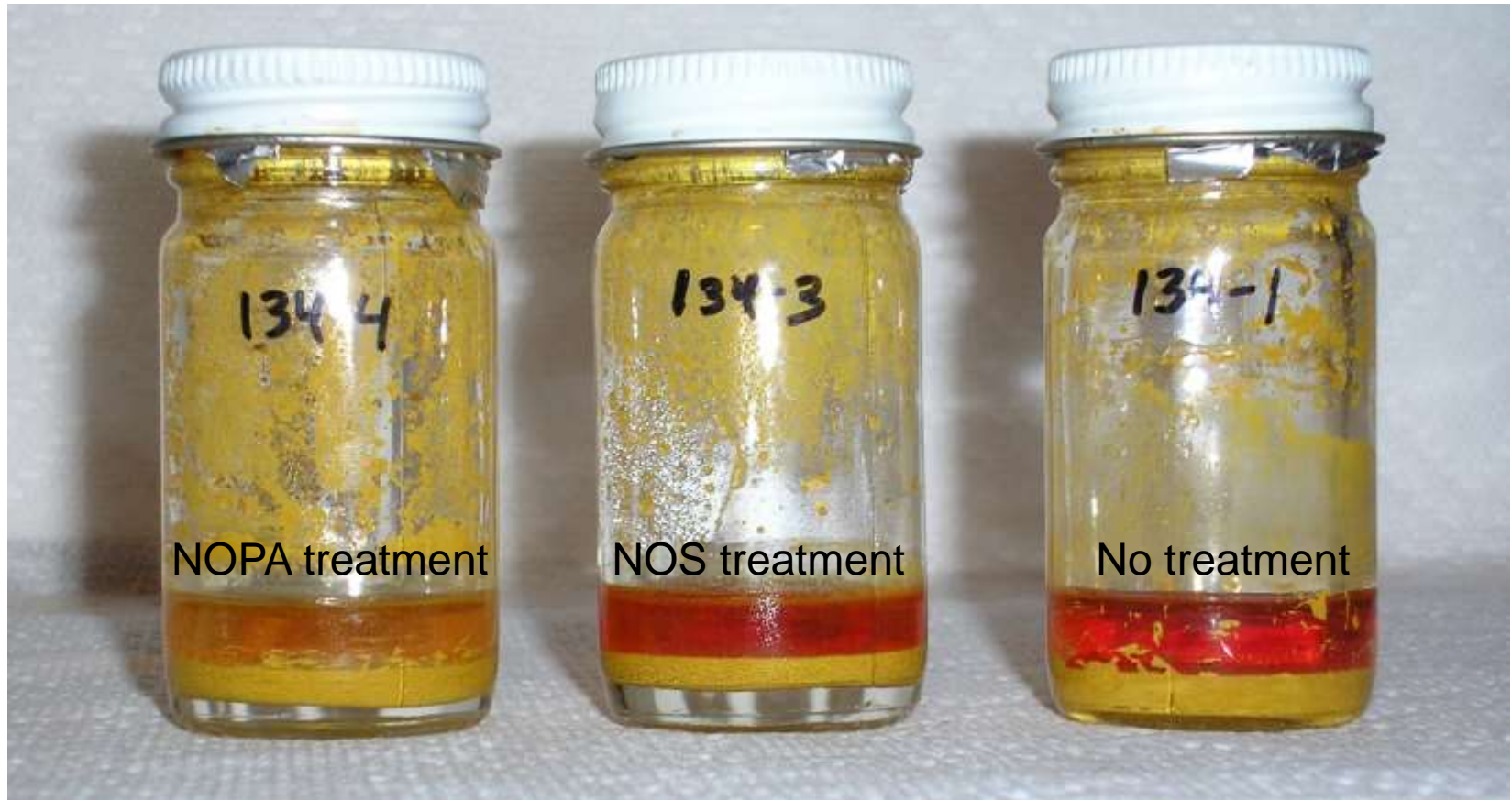


Discoloration of avobenzone will occur in the presence of treated and “as-received” yellow iron oxide pigment.

These images depict discoloration after heat aging for 50 days at 55°C.

The NOPA treated powder mitigates this undesirable side reaction.

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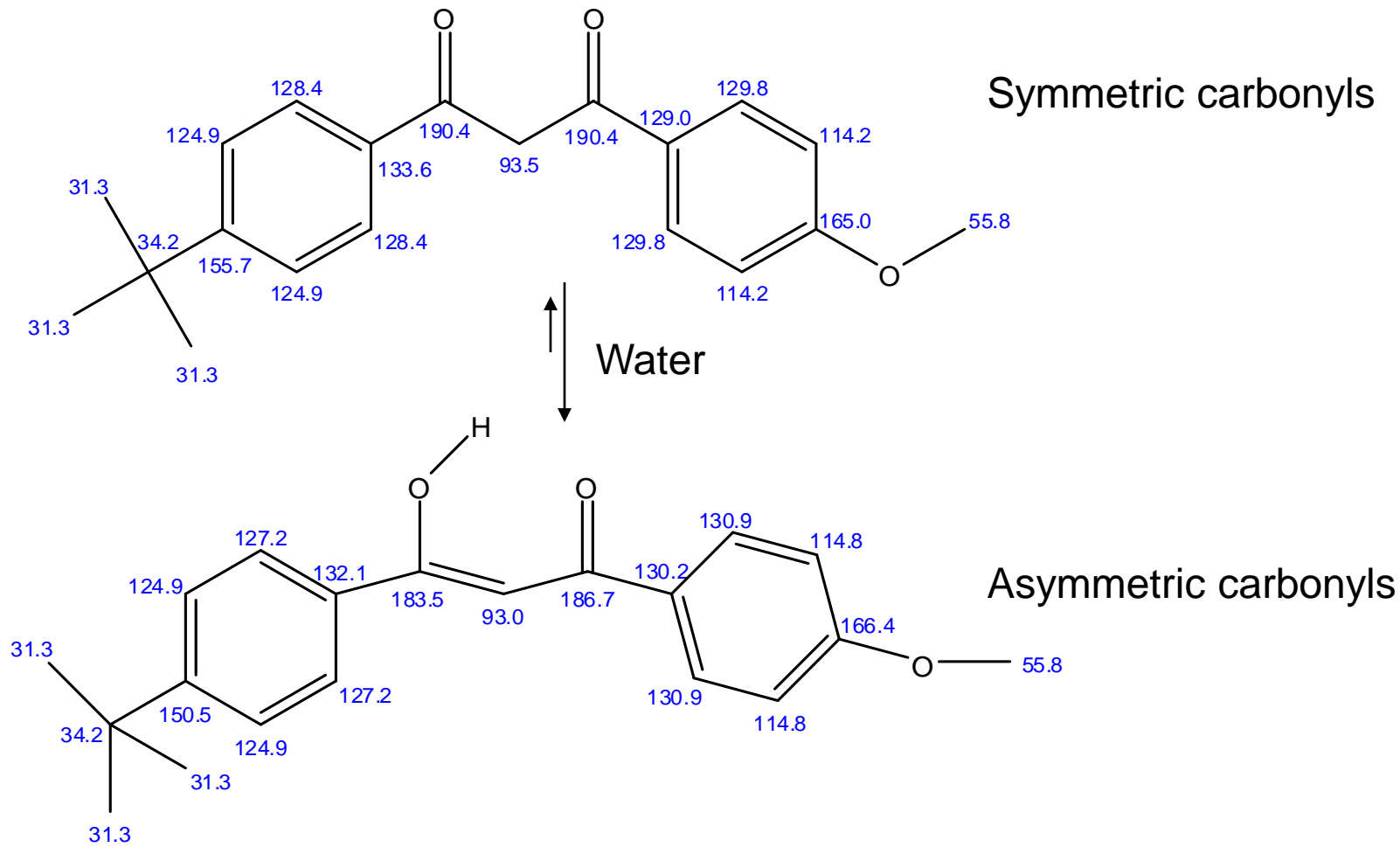


These images depict discoloration of yellow iron oxide pigment after heat aging for 60 days at 55°C, followed by continued ambient aging for 4 months.

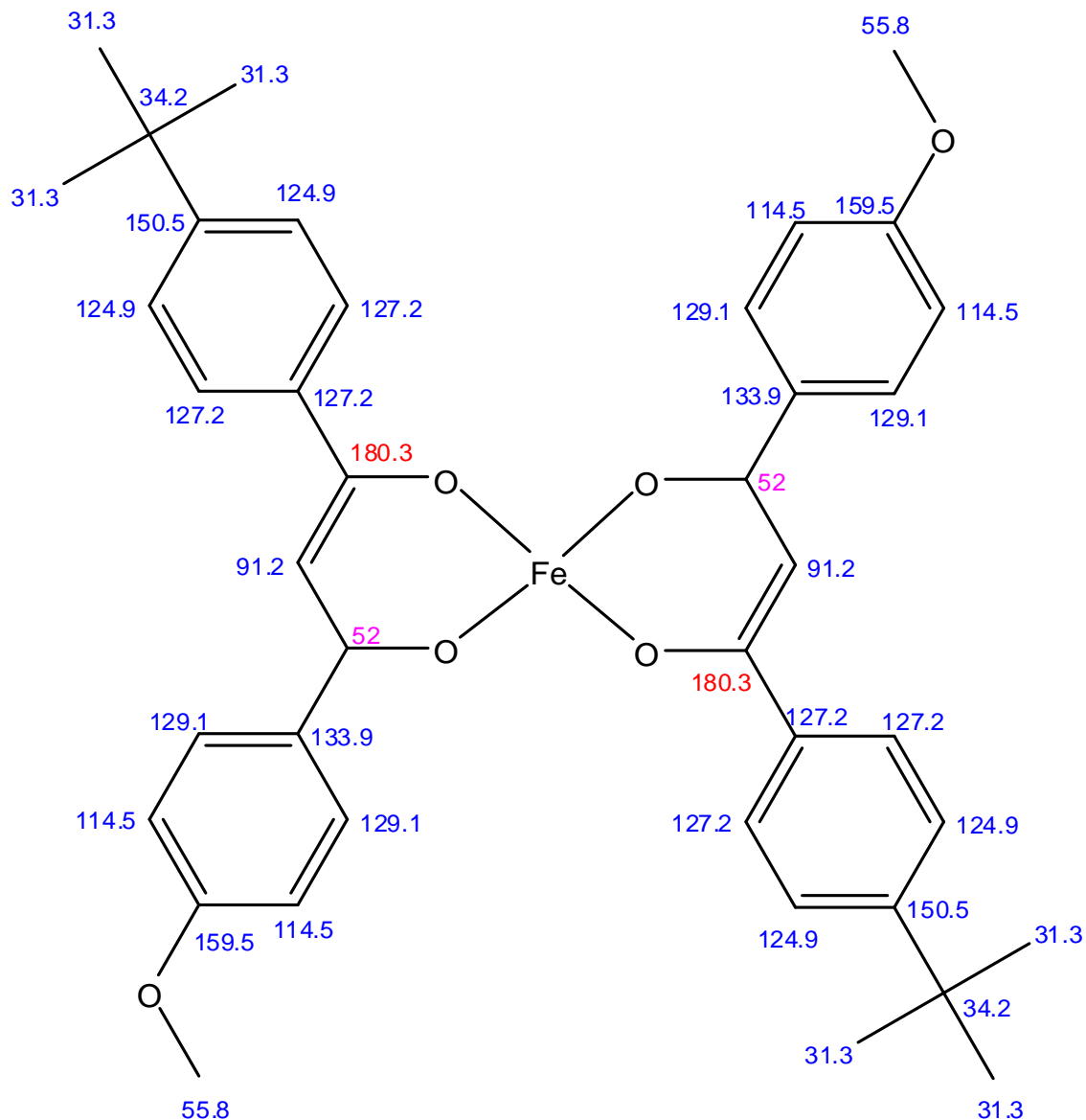
The longer-term visual benefit afforded by NOPA can be corroborated analytically via NMR studies of the caprylic triglyceride supernatants.

Tautomerisation of Avobenzone and Anticipated Effects on ^{13}C Chemical Shifts

ChemNMR ^{13}C Estimation



NMR Studies of Pigment-Sunscreen Interactions



Chemical shift calculations predict that Fe(III) chelation should produce a moderate upfield chemical shift for one of the ^{13}C carbonyl carbons, and a strong upfield shift for the second carbonyl carbon.

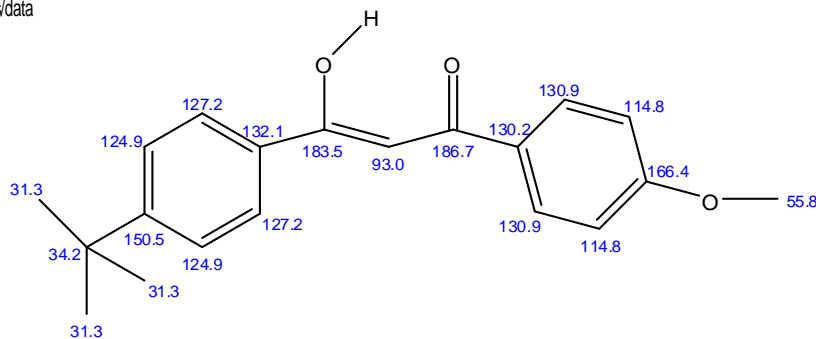
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^{13}C solution NMR spectrum of caprylic triglyceride containing 2.5% avobenzene (w/w)

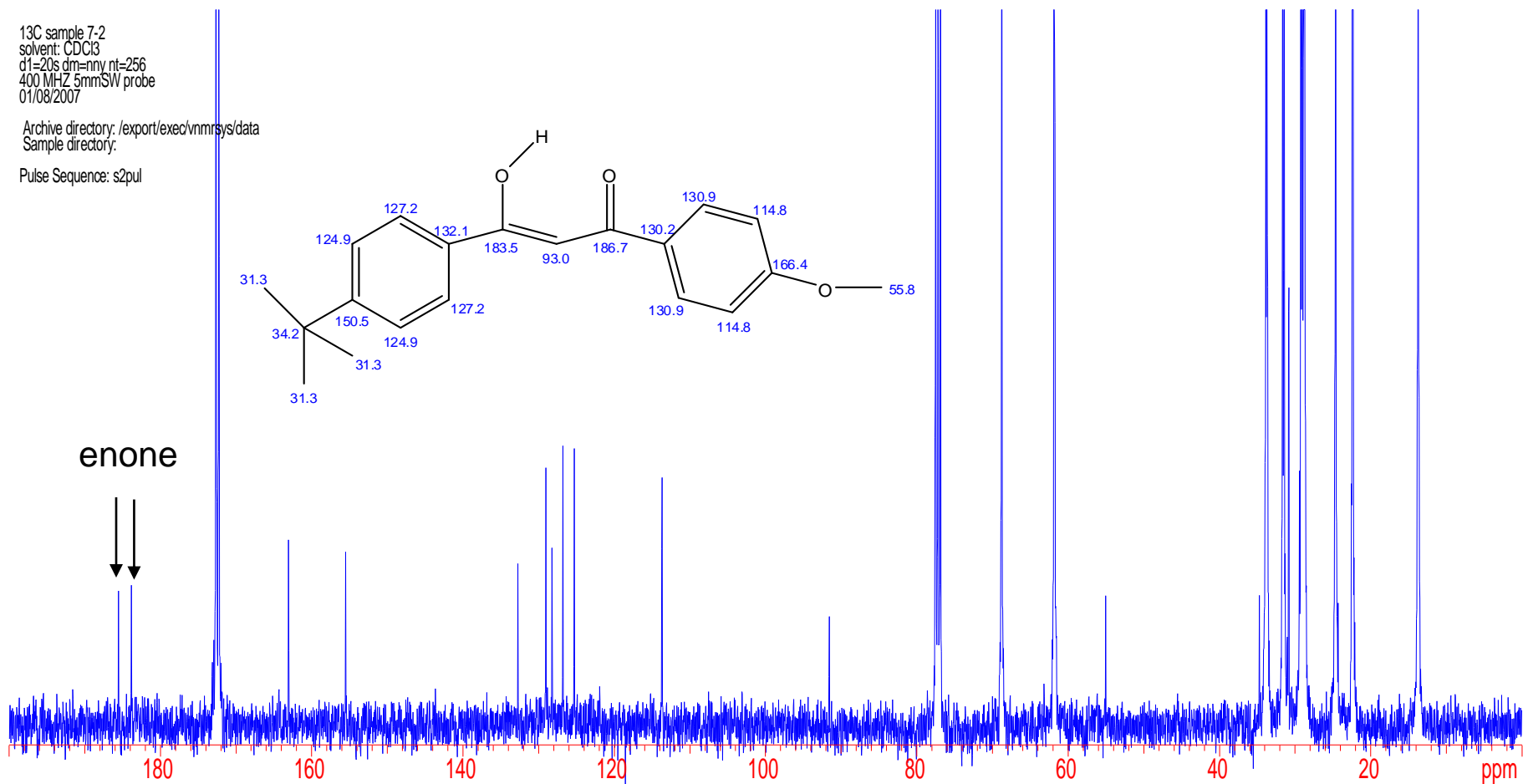
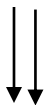
^{13}C sample 7-2
solvent: CDCl_3
d1=20s dm=nny nt=256
400 MHz 5mmSW probe
01/08/2007

Archive directory: /export/exec/vnmr/sys/data
Sample directory:

Pulse Sequence: s2pul

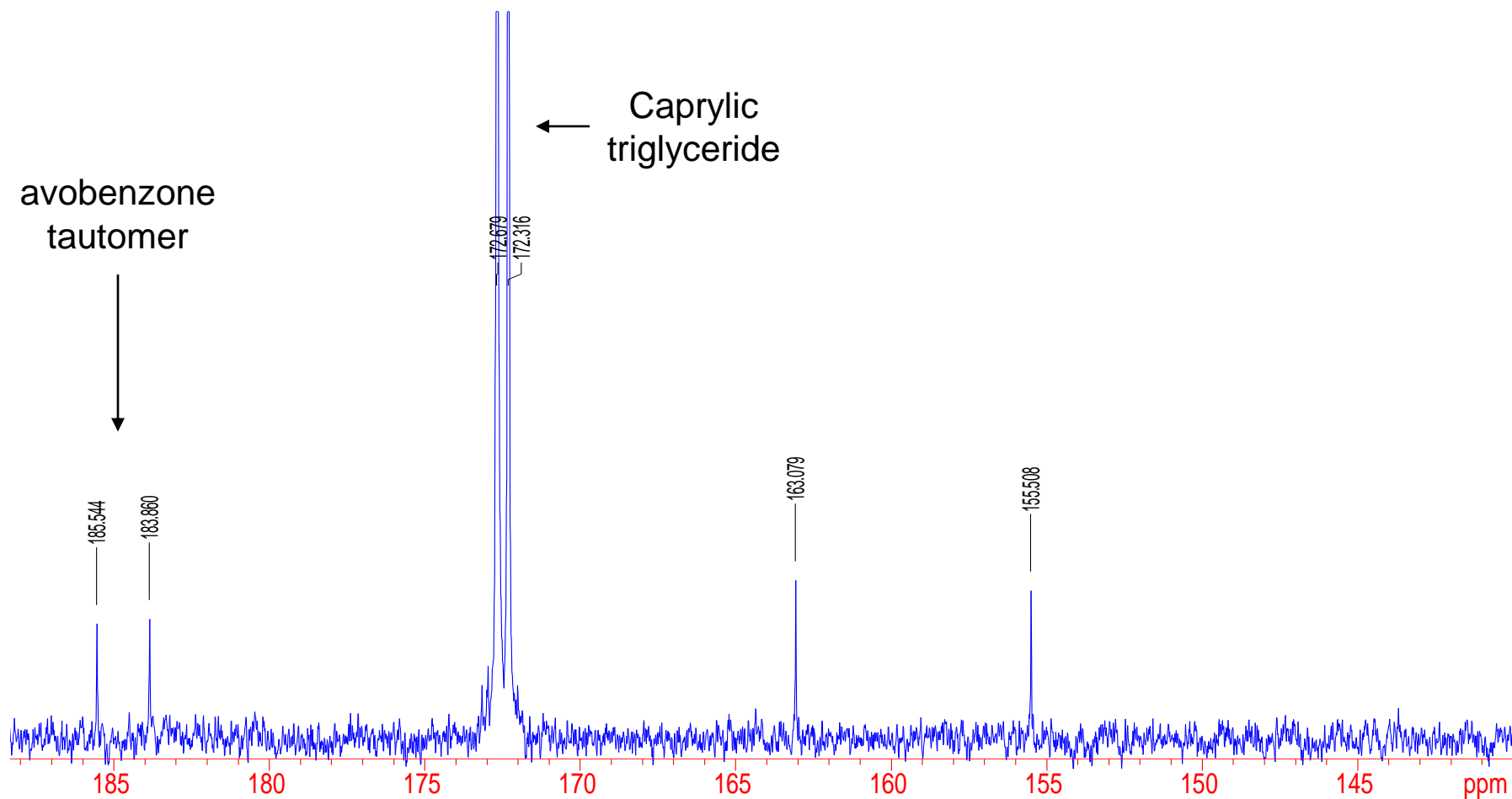


enone



NMR Studies of Pigment Sunscreen Interactions

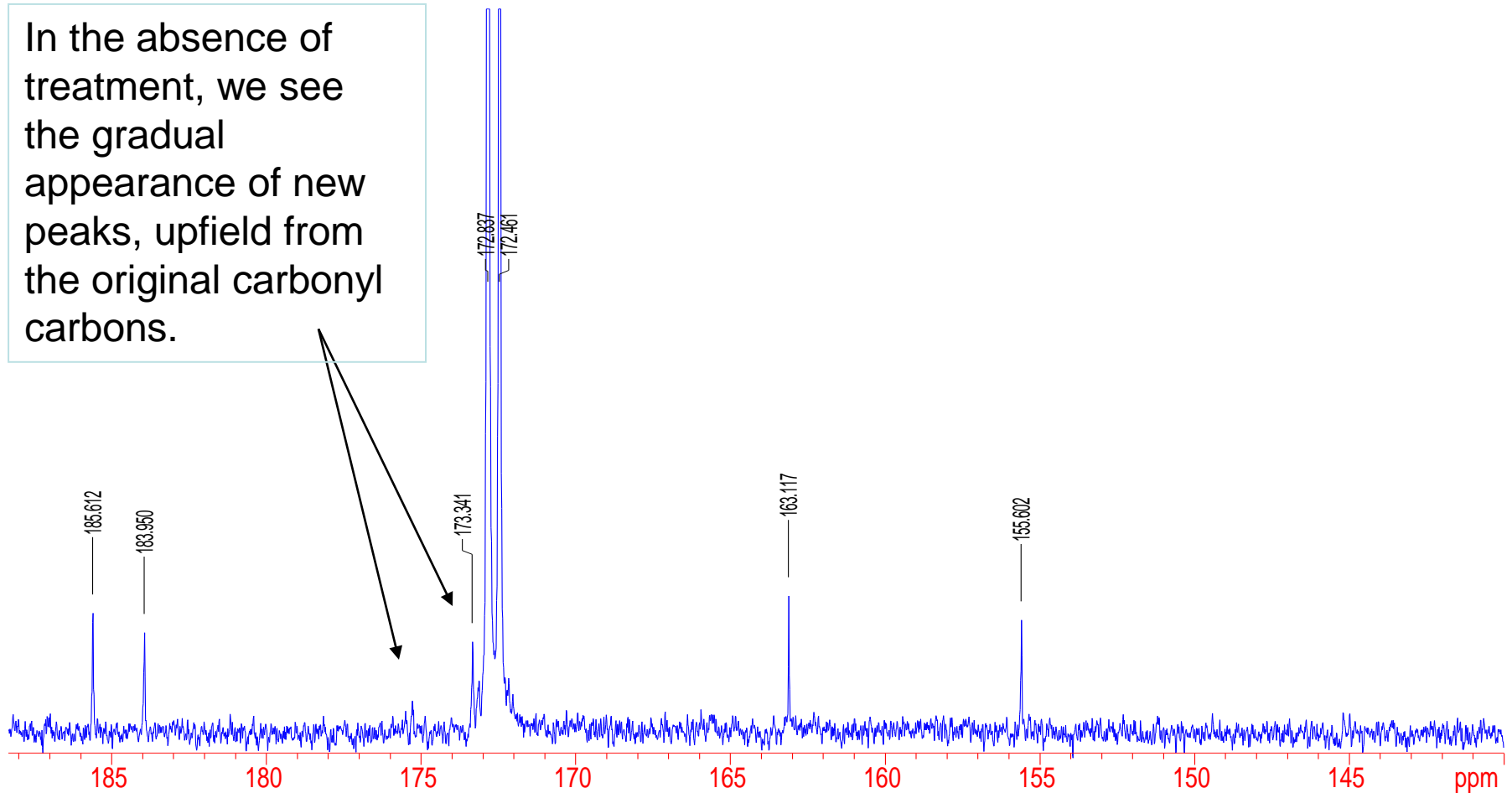
^{13}C solution NMR spectrum of caprylic triglyceride containing 2.5% avobenzene (w/w)
(expansion of carbonyl region)



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^{13}C solution NMR spectrum of caprylic triglyceride containing 2.5% avobenzone (w/w) after exposure to yellow iron oxide

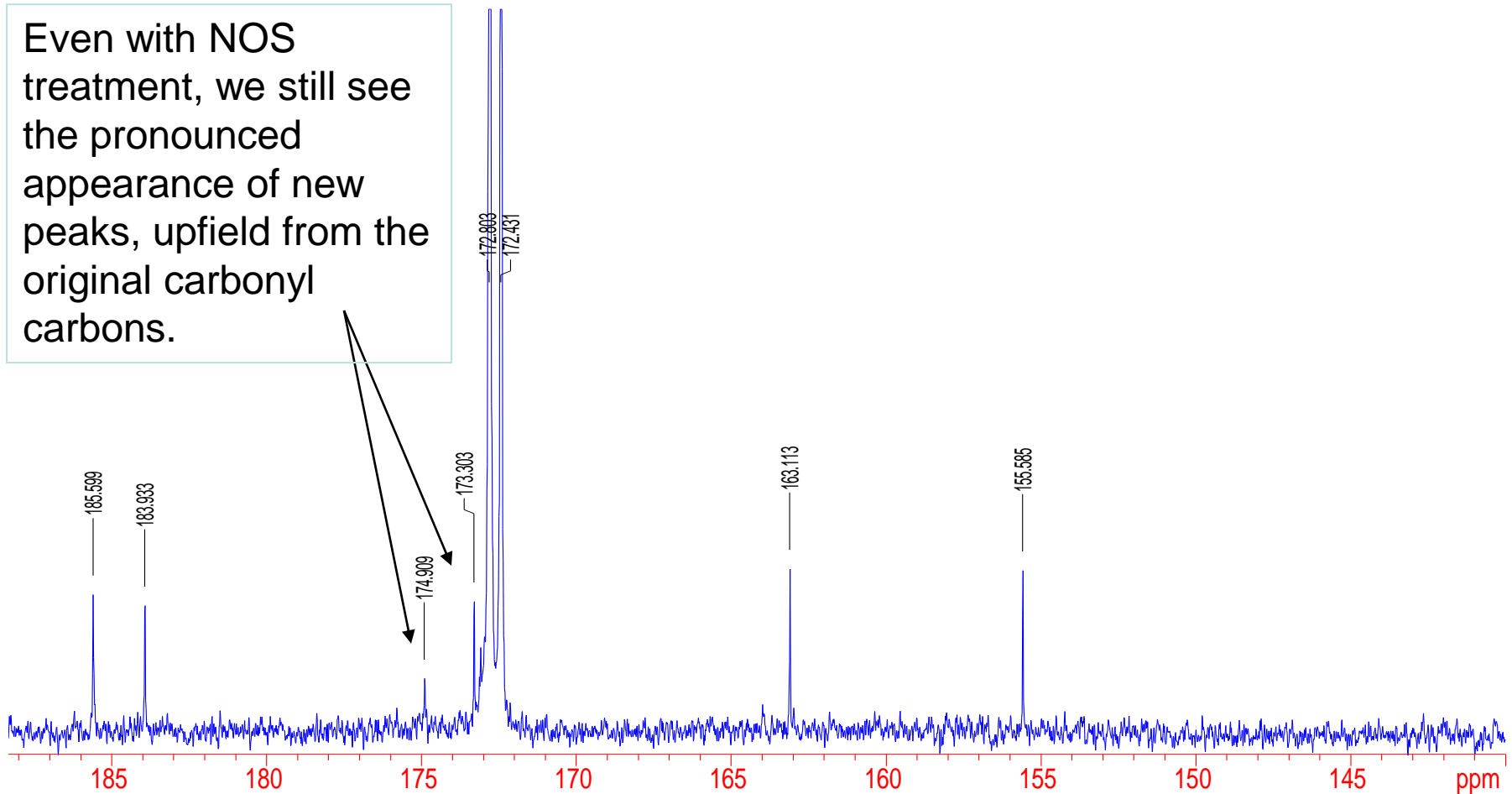
In the absence of treatment, we see the gradual appearance of new peaks, upfield from the original carbonyl carbons.



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^{13}C solution NMR spectrum of caprylic triglyceride containing 2.5% avobenzone (w/w) after exposure to NOS-treated yellow iron oxide

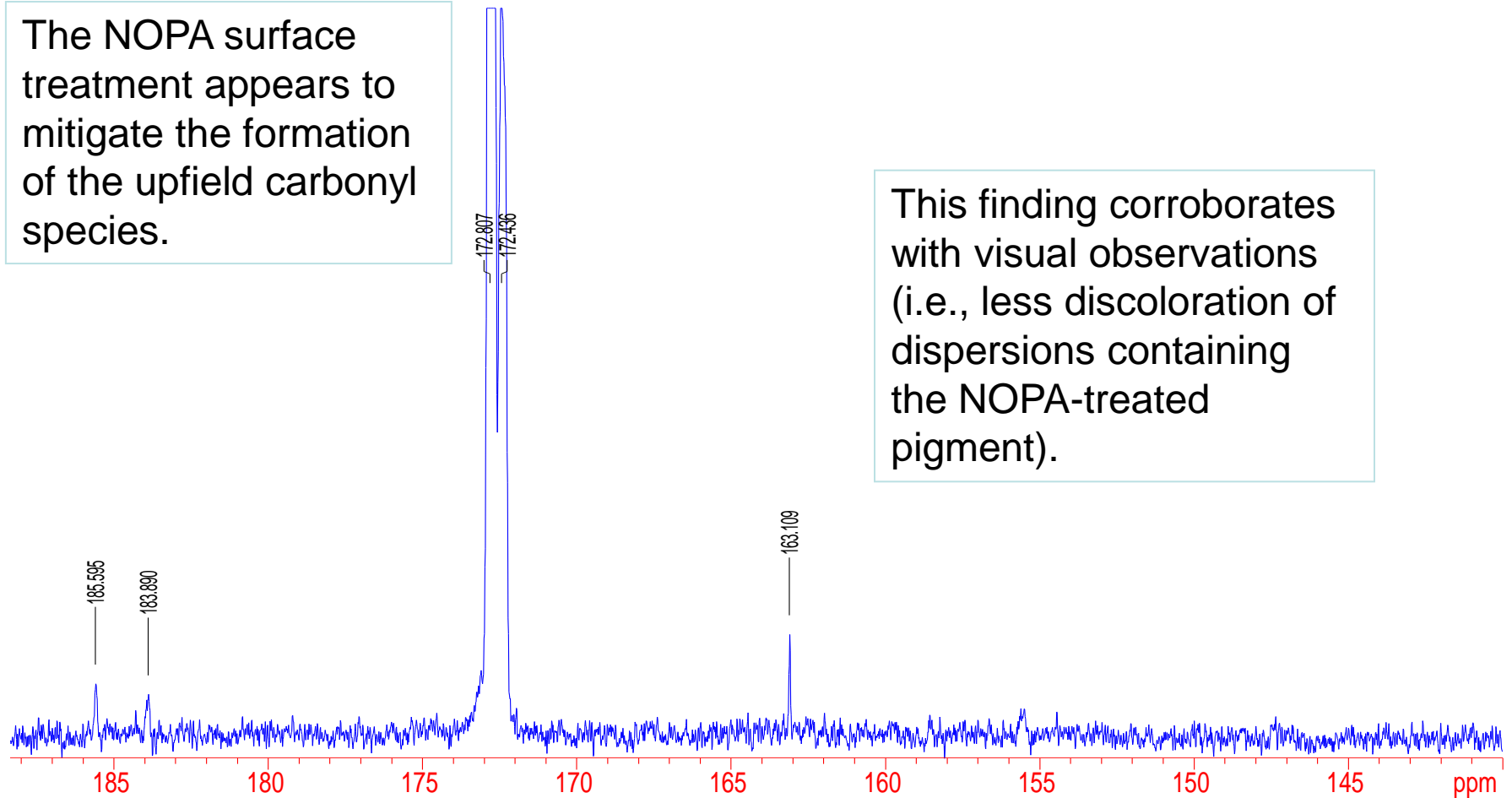
Even with NOS treatment, we still see the pronounced appearance of new peaks, upfield from the original carbonyl carbons.



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^{13}C solution NMR spectrum of caprylic triglyceride containing 2.5% avobenzone (w/w) after exposure to NOPA-treated yellow iron oxide

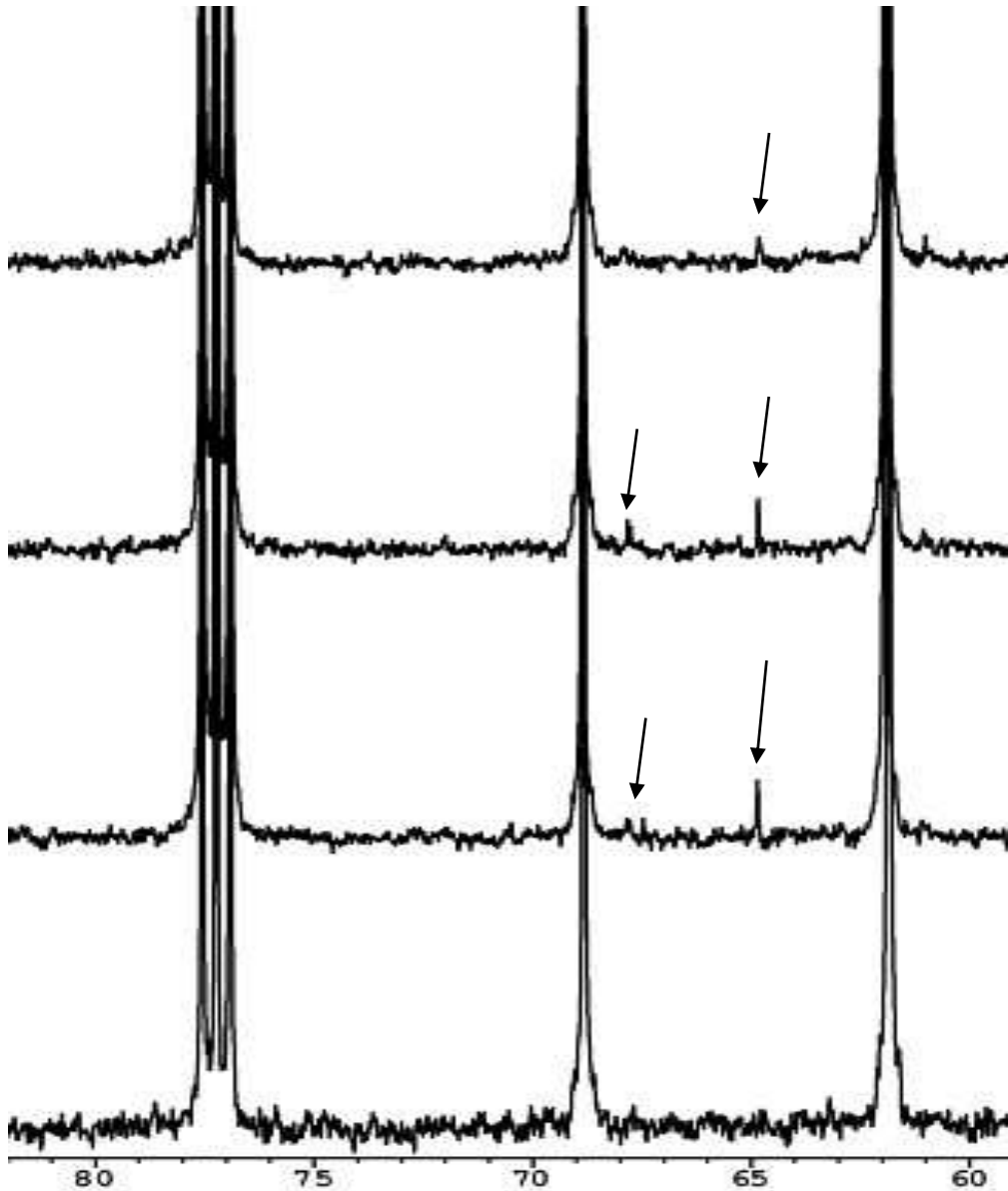
The NOPA surface treatment appears to mitigate the formation of the upfield carbonyl species.



This finding corroborates with visual observations (i.e., less discoloration of dispersions containing the NOPA-treated pigment).

NMR Studies of Pigment Sunscreen Interactions

After heat aging for 60 days at 55°C, followed by ambient aging for 4 months



2.5% avobenzene after exposure to NOPA-treated yellow oxide

2.5% avobenzene after exposure to NOS-treated yellow oxide

2.5% avobenzene after exposure to yellow oxide

2.5% avobenzene

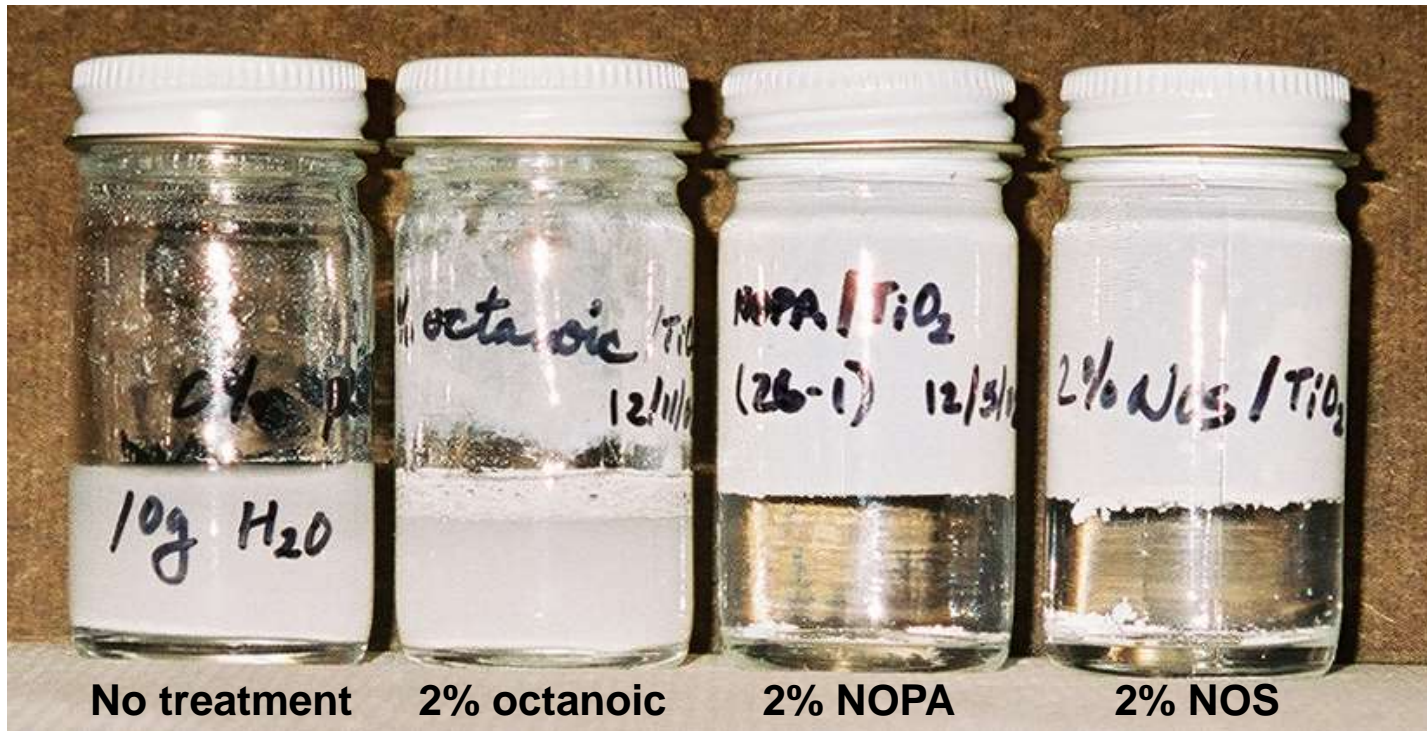
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NOS vs. NOPA

TiO₂ dispersions in water & in oil

Relative Hydrophobicity

0.05 g aliquots of each powder were individually weighed into separate glass jars together with 10 g of distilled water. The mixtures were then vigorously shaken by hand, and the closed containers were set on a horizontal surface for visual observation.



NOS and NOPA surface treatments impart hydrophobicity – an attribute desirable for creating oil-phase dispersions for water-in-oil or oil-in-water sunscreen formulations.

Relative Hydrophobicity vs. Surface Concentration – NOPA



No treatment

0.5% NOPA

1% NOPA

2% NOPA

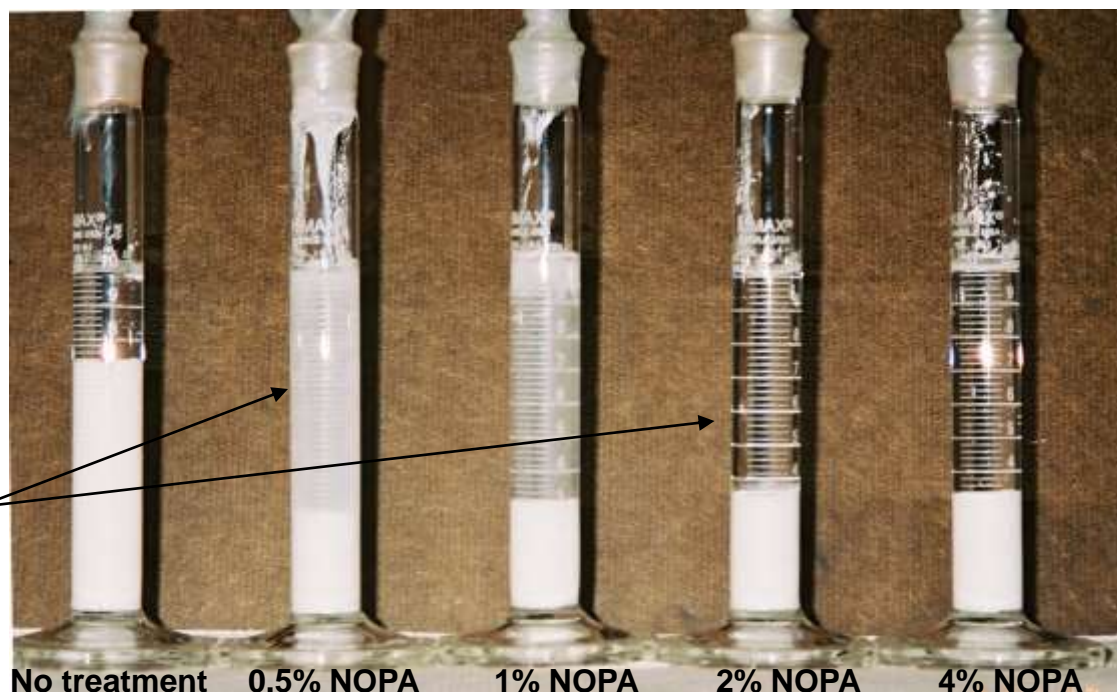
4% NOPA

surface
bilayer
formation

- Hydrophobicity is observed to improve up to a point, but a reversal occurs when the NOPA treatment exceeds 2% by weight dry powder – i.e., the powder becomes hydrophilic.
- NMR results suggest that this phenomenon is related to the presence of excess NOPA (i.e., weakly bonded NOPA that is not assembled within the chemisorbed self-assembled monolayer or “SAM”). Excess or “free” NOPA would be available to phase-invert, and to form a second surface layer with charged groups that extend into the water phase.
- These weakly bonded, “free” species are observed to appear when the total NOPA concentration exceeds the critical adsorption concentration (CAC) for SAM formation.

Relative Lipophilicity via Sedimentation

(14.28% solids in decamethylcyclopentasiloxane carrier, DC245 silicone from Dow Corning)



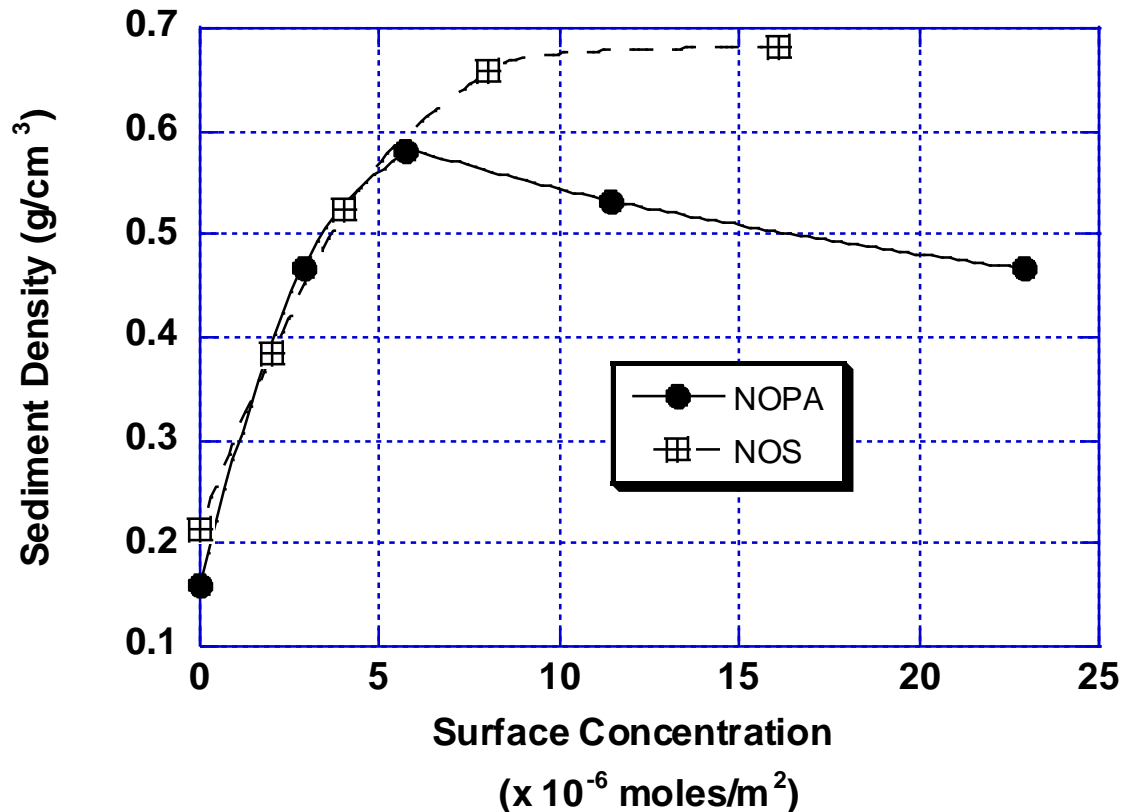
Adsorbate Concentration ($\mu\text{moles}/\text{m}^2$) \longrightarrow

The (CAC) can be interpolated between these two concentrations

- When high density powders are dispersed in lower density liquids, they tend to settle under static conditions. Less agglomeration (i.e., better dispersion) is accompanied by slower sedimentation rates and by higher sediment densities.
- The critical adsorption concentration (CAC) can be approximated by means of these types of sedimentation experiments.
- Solid state NMR can be used to study this phenomenon at a deeper level.

Relative Lipophilicity via Sedimentation

Sedimentation density (g/cm^3) of TiO_2 powder dispersed in DC245 silicone at 14.28% solids by wt. as a function of NOPA and NOS surface concentrations (mole/m^2)



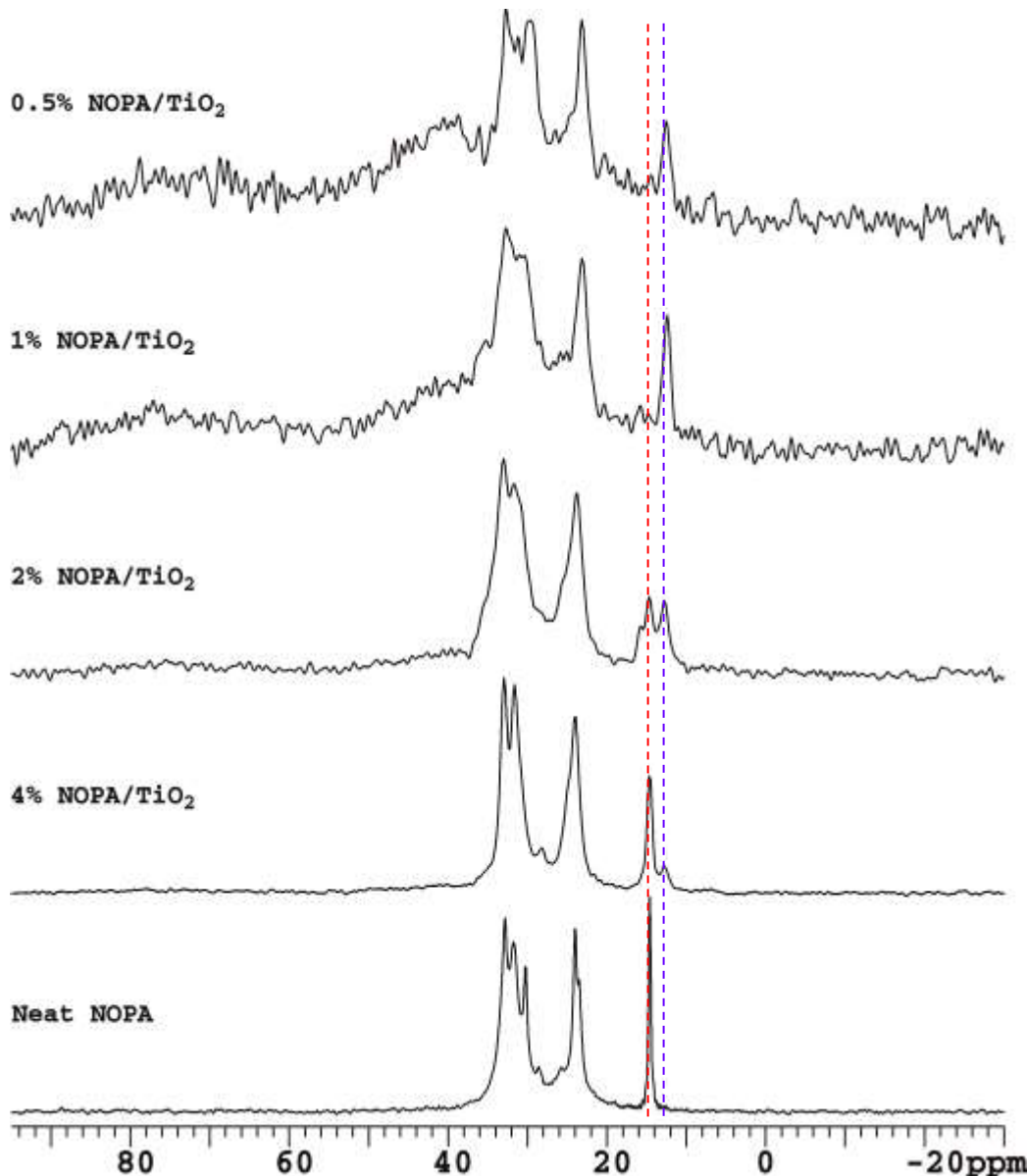
The CAC's for NOS and NOPA occur at approximately 6 to 10 $\mu\text{moles/m}^2$, a range which is typical for many chemically bonded surface-treatments on many types of inorganic powder surfaces.

NOS and NOPA appear to impart similar degrees of lipophilicity up to their respective critical surface adsorption concentrations, but beyond these concentrations, the two surface treatments behave differently.

NOPA

Self-assembled monolayer (SAM) formation

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Solid state ^{13}C CP/MAS NMR spectra

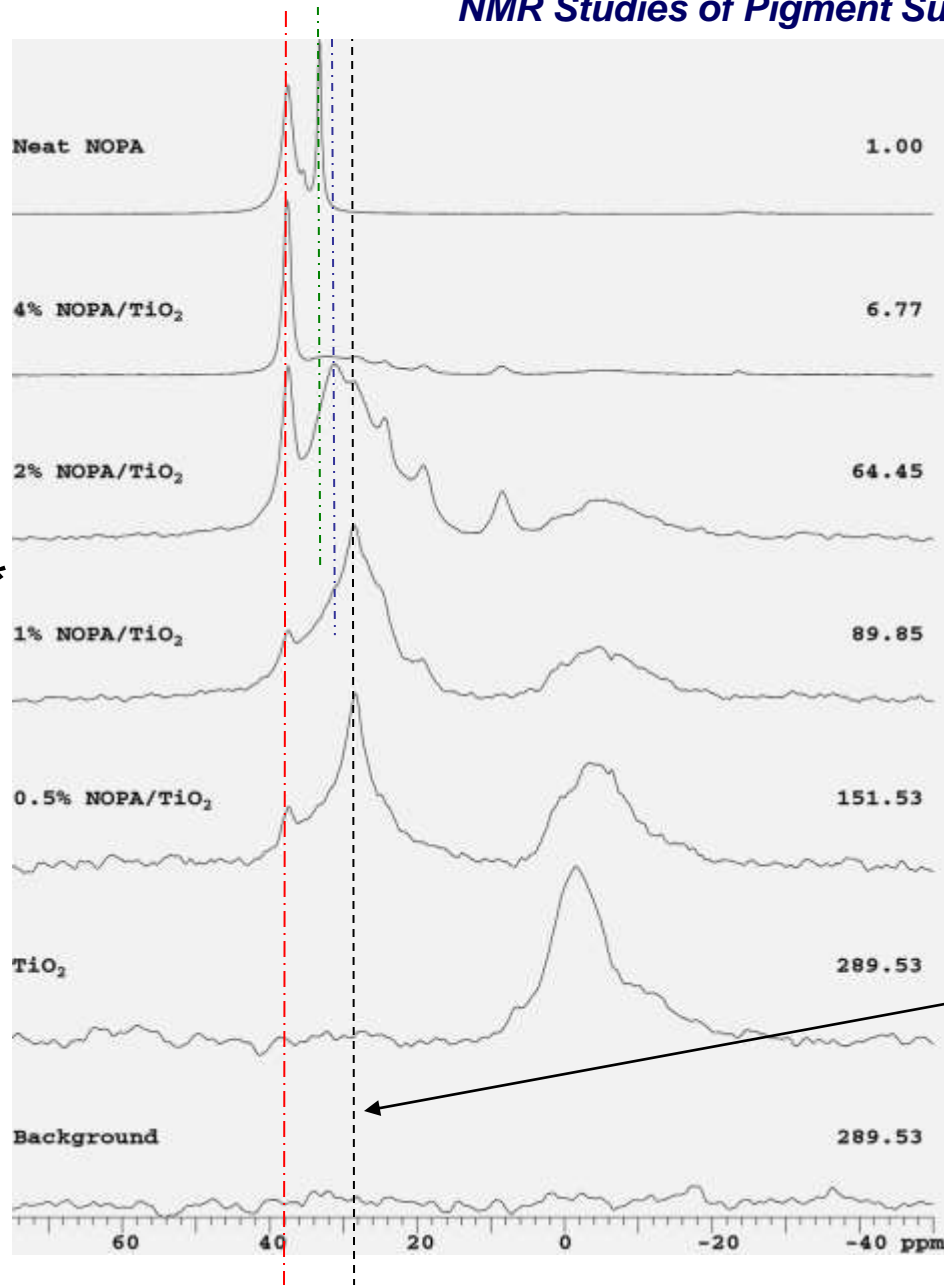
Neat NOPA, NOPA-treated TiO₂ powders, and neat TiO₂.

The methyl carbon resonance at 12.7 ppm is indicative of monolayer formation [W. Gao, L. Dickinson, C. Grozinger, F. G. Morin, L. Revin, *Langmuir*, **13**, 115-118 (1997)].

*The critical adsorption concentration from sedimentation corroborates with a change in the composition of surface structures.

A different chemical environment begins to appear at a NOPA concentration of greater than 1% and less than 2% w/w powder (i.e., when the CAC is exceeded for SAM formation).

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Solid state ³¹P MAS NMR spectra

180 second relaxation delay time

Neat NOPA, NOPA-treated TiO₂ powders, and neat TiO₂ (from top to bottom).

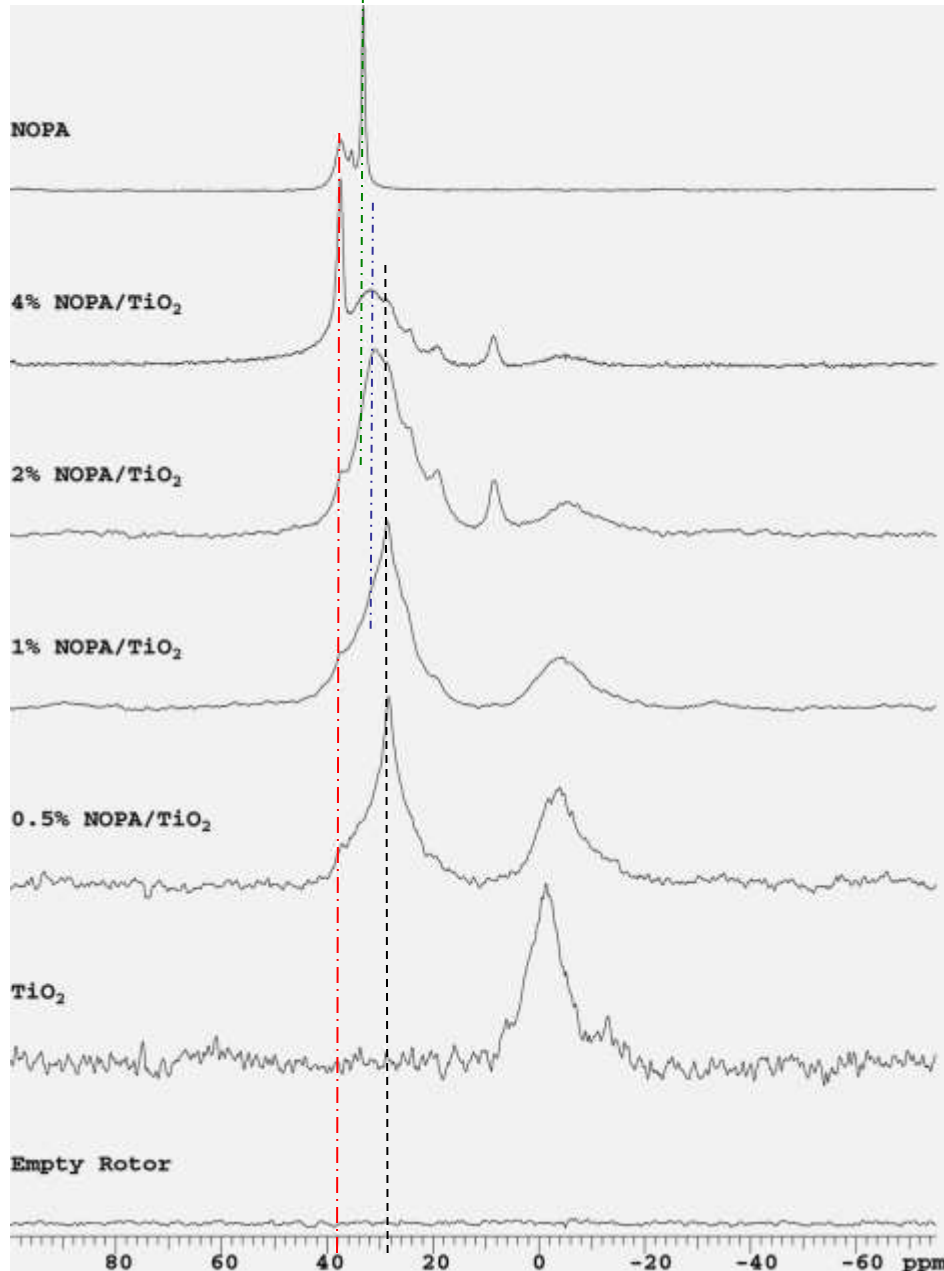
All spectra are scaled to the same height (scaling factors are listed on the right).

*The critical adsorption concentration from sedimentation corroborates with a change in the composition of surface-bound phosphorous structures.

28.8 ppm - surface-bound monodentate titaniumphosphonate ester¹ is the predominant species when NOPA is present at near-monolayer concentrations (less than 2% by weight in this case).

¹(W. Gao, L. Dickinson, C. Grozinger, F. G. Morin, L. Revin, *Langmuir*, 12, 6429-6435 (1996))

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Solid state ^{31}P MAS NMR spectra

10 second relaxation delay time

Shorter relaxation delay times tend to suppress signals that have long T_1 spin-lattice relaxation times (i.e., relatively mobile nuclei in this case).

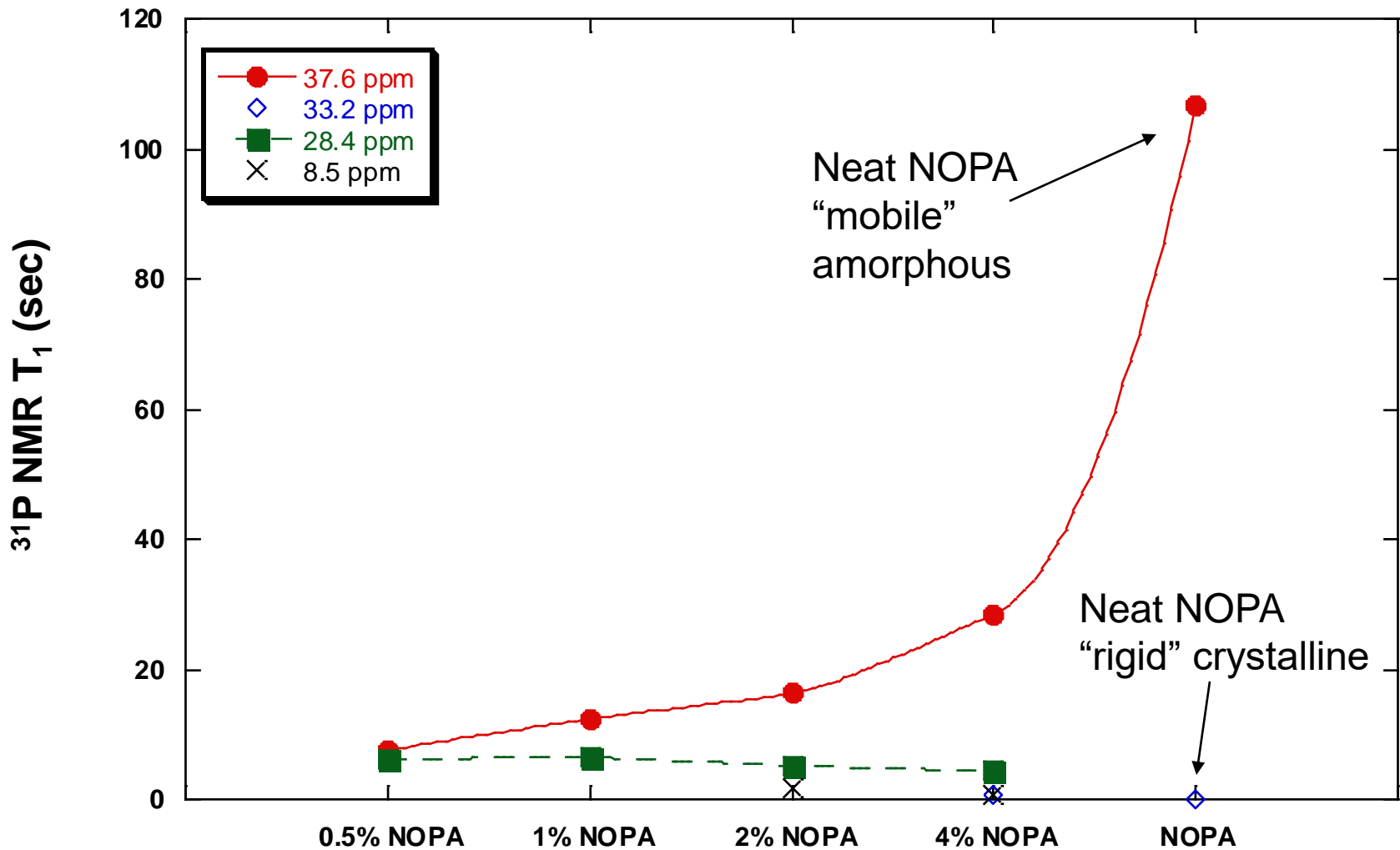
The peak near 38 ppm is characteristic of a neat NOPA component with relatively high molecular mobility.

The peak near 33 ppm is also characteristic of a neat NOPA component, but it is relatively rigid.

The surface-bound phosphonate esters are all relatively rigid (~ 31 , ~ 28 , and ~ 8 ppm).

Note that the as-received neat TiO_2 also appears to contain a surface-bound phosphonate salt (unrelated to NOPA).

Solid State ^{31}P T_1 's vs. NOPA Concentration



What happens when we add water?

Aside from oils and organic UV absorbers like avobenzone, water can be an integral component of a sunscreen formula. It is also present in the end-use environment (e.g., at the beach on a sunny day).

“Solid State” NMR techniques can be used to study dispersions of solids in liquids.

In this example, we have used solid state NMR to study 50/50 (w/w) slurries of treated and neat TiO₂ powders in D₂O.

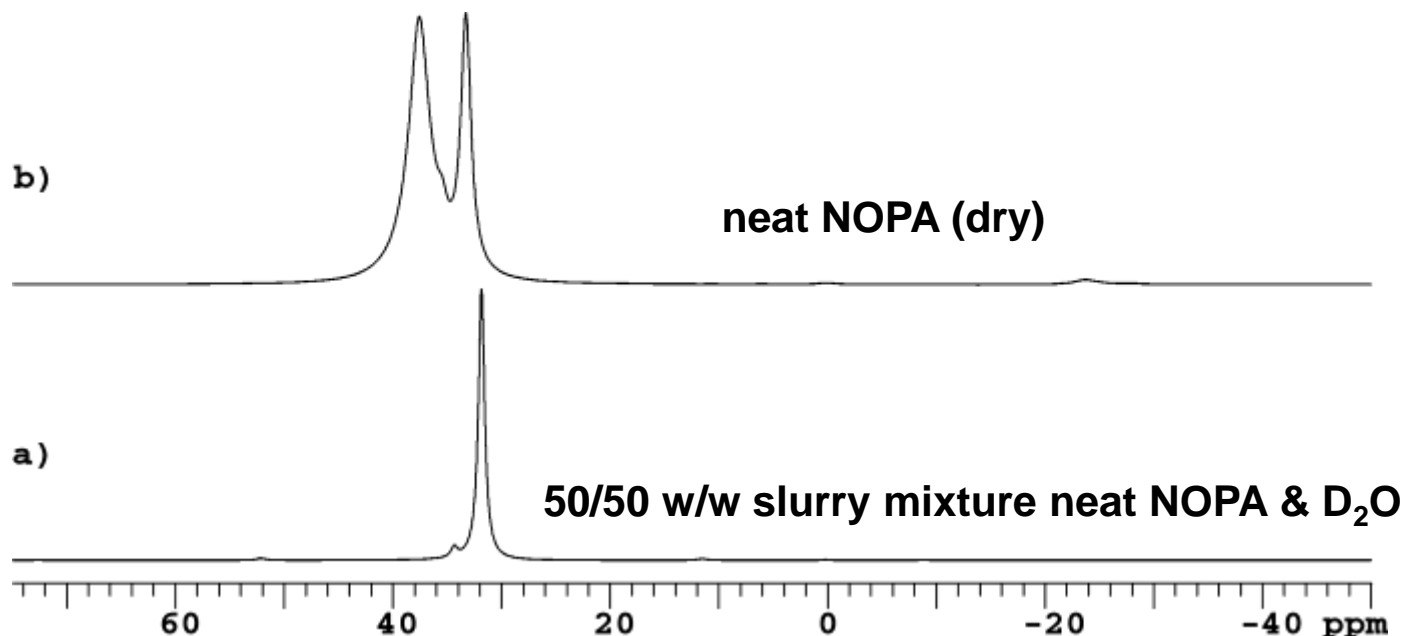
Recall that when NOPA is used at a concentration of 4% w/w dry powder (i.e., above the CAC), the material becomes hydrophilic. Why?



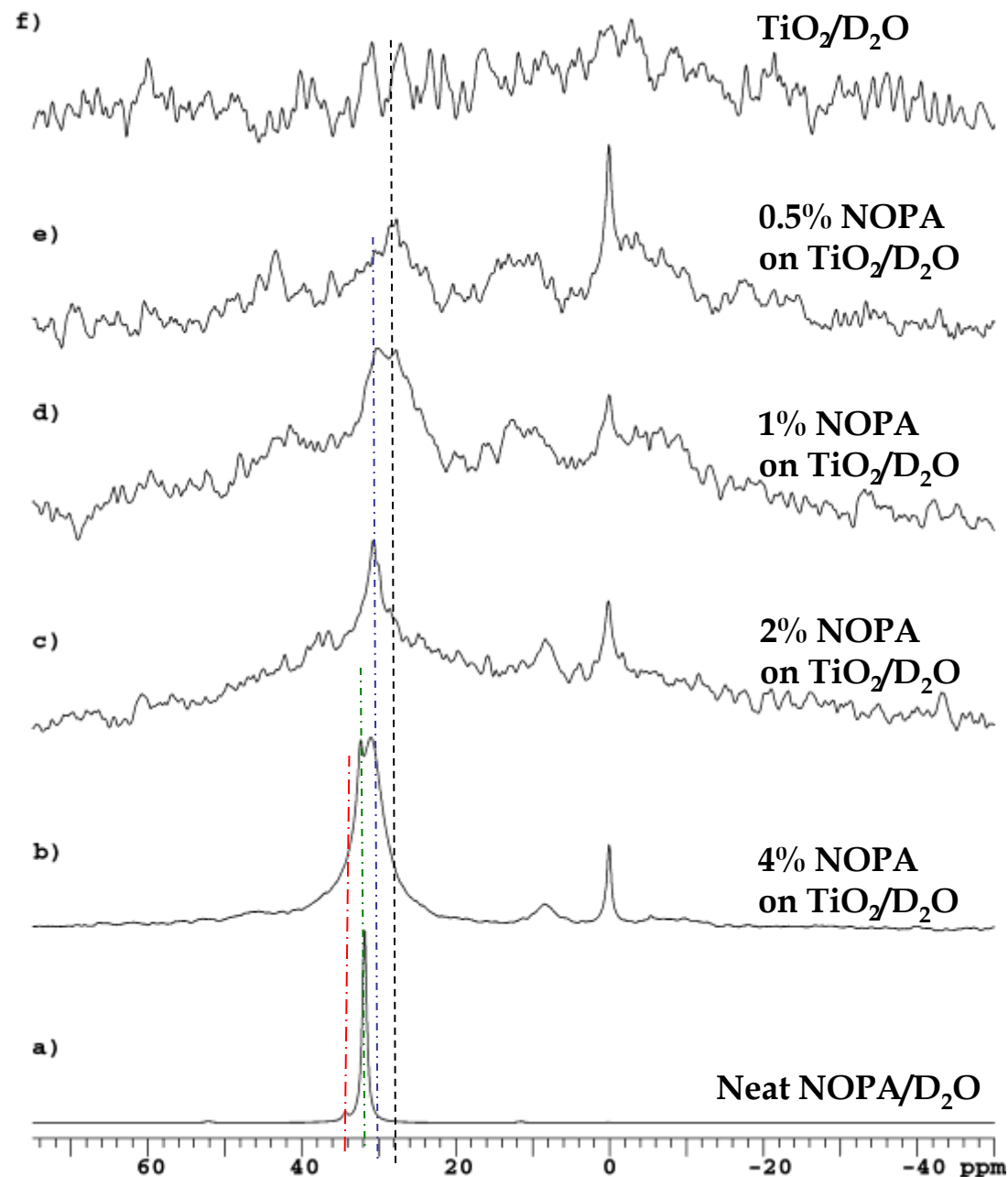
Solid-state ^{31}P MAS NMR spectra of NOPA

Experimental NMR conditions can allow for the “solid state” analysis of high-solids slurries in deuterated water.

Signal averaging with long recycle delay times allows for the detection of mobile (desorbed) nuclei, and rigid (chemisorbed) nuclei.

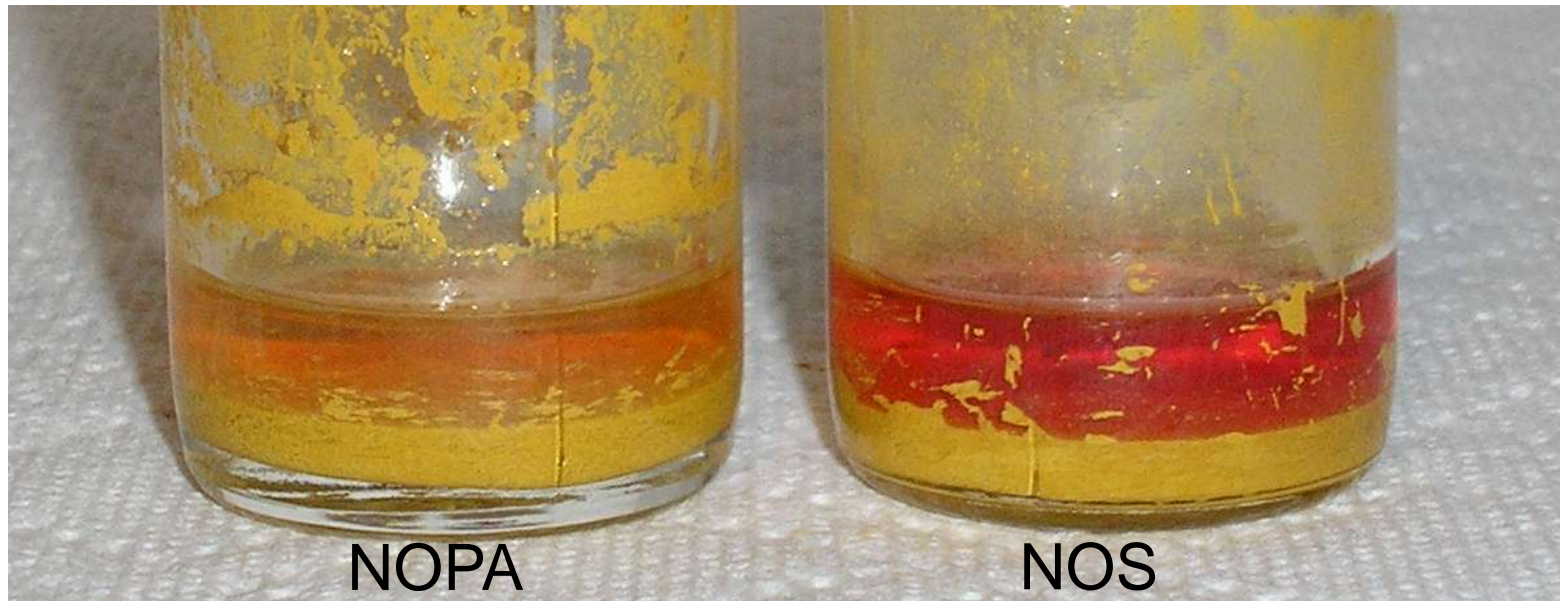


Owing to differences in mobility in the presence of water, the original NOPA peaks (~33 & ~38 ppm) appear to coalesce into a single peak with a small shoulder.



- 180 second relaxation delay (for comparison to the solid-state spectra in slide 24).
- The rigid surface-bound ester (~28 ppm SAM) and the weakly bonded ester (~31 ppm) remain chemisorbed at all concentrations.
- The non-bonded NOPA species (~38 & 33 ppm) have begun to desorb.
- Some of the NOPA species may be converted into different types of salts in the presence of TiO_2 , (e.g., the phosphonate near zero ppm, similar to the salt that was originally present on the as-received solid TiO_2).
- The 1% to 2% treatment levels appear to be the most stable, with complete SAM coverage remaining intact.
- Higher concentrations yield the more soluble species, i.e., those that can assemble into inverted bi-layers, rendering the powder as “hydrophilic.”

Recall that the NOPA treatment mitigates the unwanted beta-diketone side-reaction with Fe(III) to a greater degree than does the NOS surface treatment.



Based on the data and observations, there are several possible reasons (hypotheses) for these differences, one of which relates to diffusion.

- In the absence of a surface treatment, surface iron species become solvated through chelation with the conjugate base of the avobenzene diketone tautomer (a weak acid, $pK_a = 9$ to 10). This leads to the formation of a strong visible chromophore in solution.
- NOS polymerizes to form a 3D polysiloxane network around the Fe oxide particles. By contrast, NOPA does not polymerize, but instead, it bonds to the surface to form a 2D SAM.
- Both types of protective coatings can lead to physical diffusion barriers that slow down the solvation/chelation process.
- However, the better protection afforded by NOPA cannot be explained by its 2D SAM diffusion barrier alone, particularly since a 3D polymer network (as formed by NOS) would arguably provide a better physical diffusion barrier than a 2D self-assembled monolayer. Instead, it is likely that other mechanisms are involved.

An alternative hypothesis relates to competitive acid/base reactions.

- When the powders are pre-treated with either NOS or NOPA, a large fraction of the surface bound molecules will exist in their conjugate base forms – i.e., bonded with Fe species. This diminishes the availability of surface Fe for bonding with the di-ketone.
- Relative acidity: phosphonic acids (pKa ~ 2.6 and 7.9) > silanol (pKa ~ 4-5) > beta-diketone (pKa > 9).
- Relative basicity of conjugate base forms: beta-diketone > silanol > phosphonic acid.
- As the weakest acid in the group, the beta-diketone would yield the strongest conjugate base, giving it perhaps the greatest potential to chelate with unprotected Fe surface moieties.
- However, in order for the chromophore to form, the surface bonded protective groups would first have to become desorbed.
- In the presence of a proton source (e.g., even in the presence of a weak acid like a beta-diketone), some of the surface bound protective groups will eventually become desorbed; but in order to do so, they would first have to exchange Fe for one or more protons (e.g., a proton from the weaker beta-diketone acid).
- Being the weaker base and the stronger acid, the surface-bound NOPA phosphonate ester might be less likely (i.e., slower) to become protonated than comparative surface-bound NOS species.
- These types of competitive equilibria reactions can be further complicated by the fact that NOPA and NOS have the potential to bond in tridentate fashion with the Fe surface.
- Clearly, continued research will be needed to uncover the most likely mechanistic reasons for the differences between the NOPA and NOS surface treatments.

Possible Future Studies

- ^{13}C NMR of NOS treated powders to study the self-assembly of its alkyl chains for comparison to NOPA
- “Hydrophobicity” from the alkyl chain group’s point of view & the effect of water on chain dynamics (via ^{13}C NMR)
- The influence of acid-types and acid titration on the avobenzene-Fe interaction
- Hydrolysis of NOS together with NOPA, and co-precipitation of these species on pigment surfaces

Acknowledgments:

Dr. Todd Wagler

The University of Akron, Akron, OH

Dr. Peter Rinaldi

The University of Akron, Akron, OH

Jane Hollenberg

JCH Consulting, Red Hook, NY

Dr. Angela Parker Kaiser (artwork)

Companyia Lake Angela

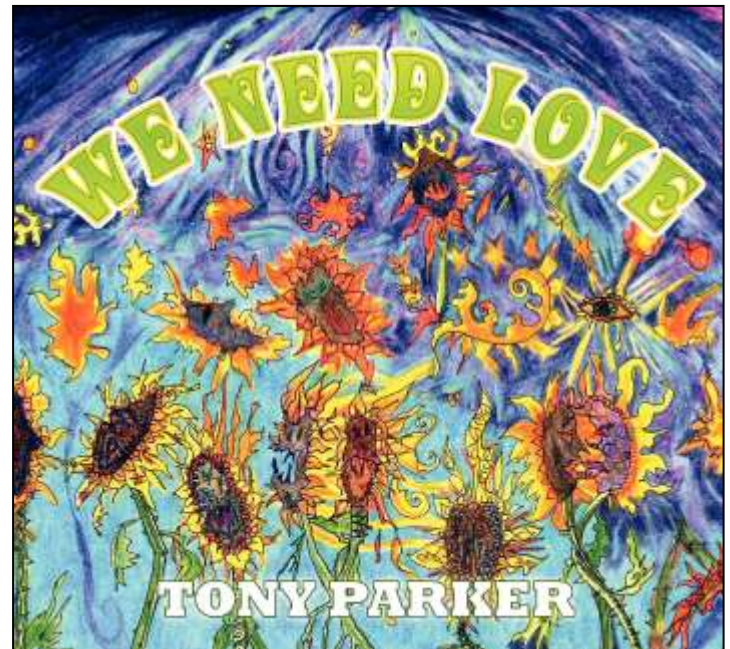
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A. A. Parker Consulting LLC specializes in polymer science, polymer processing, polymer adhesion, surface chemistry, silanes, and product development in multiple fields – spanning from wood composites & cosmetics to medical devices and surface treated musical instrument strings.

ORGANOSILANE TREATED STRINGS ***(U. S. Patents 7,476,791 & 6,348,646)***



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Tony Parker is an independent consultant and musician with more than fifty technical publications, including 30+ patents, 50+ songs, and a Ph.D. in Chemistry to his credit.

