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My Validation of Haagen-Smit's Theory of Southern California Smog Formation-The Back Story 1/16/09 Arnold Miller

The current continuing controversies origin and control of greenhouse gases brings to mind the similar controversies about the origin and control of smog in Southern California back in the 1950s through the 1970s. I played a modest role at a critical point in this earlier controversy. In hindsight, it is instructive to look at this small adventure in terms of the regional smog picture was at the time.

A significant digression occurred in my life early in 1955. Francis Blacet called. He was a world-renowned photochemist and my PhD thesis advisor at UCLA. He wanted to know if I active in photochemistry among my current work at the Illinois Institute of Technology Research Institute (IITRI). I replied in the negative. "Good", he happily responded.

Francis then proceeded to ask if I would come to California for six weeks to see if I could independently validate the groundbreaking work of a California Institute of Technology (CIT) scientist Arie Haagen-Smit. Haagen-Smit concluded that smog in California came from the photochemical reaction between unburned hydrocarbons (from auto exhaust, refineries, and chemical plants) and nitrogen oxides (again from auto exhaust and other sources of combustion). Haagen-Smit's supporting research techniques were intuitive and novel. No one was able to independently validate his work and his strong conclusions.

"Why go to Chicago to get a photochemist when there were so many good ones in LA," I asked. He replied that Southern California is the scene of a major industrial conflict. Photochemists were either working for the oil and chemical companies or were environmentalists. Industry said Southern California smog was a fact of nature, not an industrial blight. Haagen-Smit's published conclusions showed smog was manmade, with autos and refineries the principal culprits. Industry photochemists could not replicate his work. Blacet had to go afield to get a credible professional to resolve to resolve the issue.

At that time, the only governmental body involved in air pollution in LA was the weak and underfunded Air Pollution Control District (APCD). To shore up the knowledge base, an independent industry funded group, the Air Pollution Foundation (APF), was created in 1954. APCD had sponsored some of Haagen-Smit's original findings and supported his findings.

In those years, Stanford Research Institute (SRI) had an Air Pollution Control Center research project laboratory in Pasadena. The Western Oil and Gas Association sponsored this work for over seven years. The American Petroleum Institute was also a sponsor. They could not replicate his results.

I accepted the Blacet's offer. APF gave IITRI a contract for my services and I was off to Cal Tech for six weeks to resolve the issues.

I arrived in the Los Angeles Basin in early 1955 in the midst of still another series of smog attacks. There was such a note of panic about the gross environmental conditions

in the LA Basin that California Governor Knight convened a special committee of renowned medical leaders to advise him. They subsequently reassured him and the community at large that smog was a passing irritant, not dangerous to health. The primary causes of smog were deemed to be unknown, and each industry stakeholder stated their individual contributions to smog were insignificant.

At that point in time Professor Haagen-Smit was principally renowned for his work in the chemistry of plant-derived hormones. Photochemistry was not his field of life study. As a Pasadena, California resident he was just plain angry at living in an air-polluted sewer. He intuitively believed smog was primarily generated in downtown Los Angeles in the morning rush hours from the photochemical reaction action of sunlight on hydrocarbons and oxides of nitrogen from automobile exhaust. The smog (ozone) then drifted over later in the day to submerge his pristine community. He entered into atmospheric photochemistry as a concerned technically trained citizen!

Meeting Haagen-Smit in his Cal Tech laboratory for the first time was an experience. His presence filled the room. The discussion was initially guarded. Was I truly independent, or was I a tool of industry polluters?

With a prophet's fervor he sketched out his work and what appeared as very clear, definitive findings. He reported and demonstrated examples of photochemical reactions for a series of synthetic mixtures of nitrogen dioxide and hydrocarbons in the fractional to low parts per million (ppm) range in both oxygen and air resulting in production of oxidizing smog (ozone). He had presented talks giving the photochemical reactivity scale of a series of hydrocarbons in the presence of oxides of nitrogen, all in the fractional to low ppm range in reported 1954.

Even with these specifics, industrial laboratories were refusing to recognize what he felt was the obvious. The neighboring SRI Laboratory in Pasadena recognized the photochemical origin of smog, but did not know or identify the significant sources. They could not reproduce his results by any means at their disposal or by using his experimental techniques. Why?

Haagen-Smit's CIT laboratory was like no other photochemical research lab I had ever seen. He used large round bottom flasks for reaction chambers and fluorescent light fixtures as artificial sunlight sources, and injected small quantities of reactants with hypodermic syringes into the chambers.

Since his funds were limited, he was not able to acquire the expensive analytical instruments extant at the time to attempt measurements in the fractional ppm range. This didn't deter him.

Since high air pollution levels causes severe tire cracking in California, he intuitively used bent strips of tire rubber as suspended by nylon cord in the reaction chamber as an indicator. The total measured lengths of the cracks from a test strip were deemed to be proportional to amount of smog produced in the specific experiment.

Tables in the laboratory were neatly covered with labeled rubber indicator strips carefully measured to determine the ozone produced. His published notes gave the composition of the commercial recapping rubber used in all of his experiments.

I proceeded to see if I could repeat his full range of experimental results in his laboratory to see if the results supported his vital conclusions as to the origin of Southern California smog. I planned next to ascertain why his results could not be reproduced in other facilities.

I went to work and repeated his work carefully any number of times with many different parts per million (ppm) compositions and got the same results. After measurements of the cracks on each specific stressed rubber strip following each experiment, the results mapped Professor Haagen-Smit's notebook and published results. All photochemical experiments that generated ozone were run at concentrations of reactive hydrocarbons in the 1-ppm range found in Southern California air.

Interestingly enough, reactions of hydrocarbons in the 700-ppm hydrocarbon range under the same experimental conditions with Haagen-Smit's procedures resulted in no cracking, no ozone produced. At higher concentrations not found in the atmosphere, the photochemical reaction is quenched.

Some five miles away from Cal Tech was the SRI laboratory. After time working in Haagen-Smit's laboratory, I called over to SRI to arrange a visit with them and hold technical discussions. I was well received and we reviewed their work on the genesis of smog and their unsuccessful attempts to replicate Haagen-Smit's results.

The laboratory was handsomely equipped with the best analytical instruments, including white-optics folding path spectrophotometers to monitor reactions as they took place in their photochemical chambers. The photochemists on the staff that I met were well trained and open in the discussions.

Since the best commercial spectrophotometers of the day couldn't make measurements at the extremely low ppm range of atmospheric smog environment, SRI had to run their experiments at much higher concentrations than found in nature. In this case, Haagen-Smit's intuitive detectors were useful where advanced scientific instruments couldn't go.

Much to SRI overt disdain, they had set up a system approximating Haagen-Smit's experimental procedures with stressed tire-rubber strips and at the same concentrations used as given in his publications. They could produce no photochemical reaction, no smog. The visit to the SRI lab was productive. One part of the puzzle solved. SRI was not aware of Haagen-Smit's findings that the photochemical production of smog is quenched at very high concentrations, not found in nature. Stayed the neutral observer, and did not pass on any new information.

Haagen-Smit was not too happy with me when he learned, from me, of my visit to the SRI facility. The enmity between the two laboratories was palpable. Neither had visited each other's laboratory (short miles apart). Each questioned the validity other's work. It was not pleasant. Years later I found the CIT published year 2000 oral interviews with Haagen-Smit's widow, Zus, where she still spoke of the deep pain generated by SRI's

public disparaging of his scientific work. Understandably then, because of my visit cross-town, it took a few days to regain his confidence as to my continued impartiality.

I turned to close examination of the rubber composition and its use. Unbeknownst to me, I found that his assistant ran a solvent extraction (with a Soxhlet extractor) on batches batch of commercial tire rubber strips to remove the presence of the previously unknown antioxidant in the tire rubber before use as smog detectors. I ran duplicate photochemical reactions with extracted and non-extracted stressed rubber strips, the resultant smog was detected with extracted rubber strips, none detected with non-antioxidant extracted rubber strips.

This extraction step was not in any of Haagen-Smit's published work. Neither was the presence of an antioxidant component indicated in his published composition of the designated commercial tire blend. Haagen-Smit's response was that any good chemist would know you have to remove the antioxidant to use rubber as an indicator of oxidant.

SRI's inability to reproduce the Haagen-Smit stressed rubber technique was solved.

The full details of my findings substantiating Haagen-Smit's work were given to APF in form suitable for publication.. The results Themselves were immediately disseminated to the scientific and political community... Haagen-Smit's theory and experimentation as to the sources of photochemical smog in Southern California were validated. All this occurred early 1955.

The APF was loath to see published direct comparisons of Haagen-Smit's work at atmospheric concentration with SRI's work at elevated concentrations not found in nature (where the reactions are quenched), as well as the revealing the missing step in Haagen-Smit's presentations and reports on the removal of antioxidant present in the commercial tire blend. Even though his published composition of the commercial tire rubber did not show an anti-oxidant as an ingredient, the total lack of face to face communication between SRI and Cal Tech precluded picking this up.

The APF folks did not want to neither antagonize SRI nor their sponsors Western Oil and Gas Association, who might be financial supporters of the APF. In addition, APF did not want to antagonize Haagen-Smit for his omissions in his milestone papers. So, they asked that I not formally submit my full paper for publication, go back to Chicago and set up a smog lab study to do more work with a bit of face saving cleanup...hence the one-year delay publication in Science. The work in Chicago was derivative, but it satisfied the sponsor's perceived needs with a formal straightforward publication.

So, working with both camps, I found out the missing flaws in both endeavors, subsequently validated without question Haagen-Smit's work as to the origin of Southern California smog. California was in the lead, off and running in developing technological and legislative smog-reduction measures. Haagen-Smit technological greatness was well recognized worldwide and he continued for a number of years in active leadership on many fronts in the battle against air pollution.

It was my good fortune to have intersected with this unique scientist at such a critical time.