Synthesizing Oils Is a Slippery Job

The coming generation of high-temperature automotive engines will bake today's best lubricants into carbon residue, so researchers are looking for new synthetic oils that can take the heat

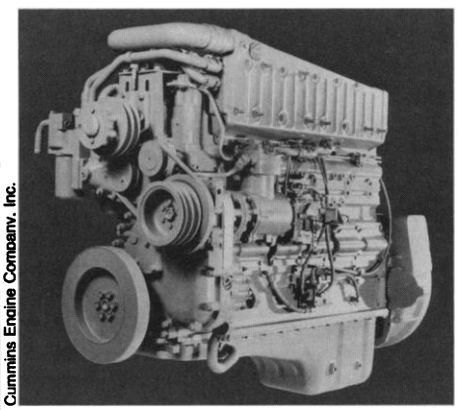
WHEN PIONEERS CROSSED THE PRAIRIES in Conestoga wagons, animal grease was all the lubrication they needed to keep the wheels turning. And when the Model T revolutionized transportation, crudely refined petroleum was more than enough to keep the car's four pistons pumping smoothly. But things aren't so simple anymore.

Automotive engineers are working on a new generation of engines that will pack more power into less space and use less fuel than today's models, but they have a problem. The planned engines will operate at temperatures much higher than those of conventional engines, higher even than the engines that power jet aircraft, and not even the best of today's oils can survive at those temperatures. Until recently, however, no one had given much thought to developing advanced lubricants that can take the heat.

"This whole area [of lubrication] has been neglected while mechanical engineers went about super-detailing their engines," says Al Jung, a materials scientist at Akzo Chemicals, Inc., in Dobbs Ferry, New York. "The limits of performance of conventional oil have been exceeded. Now what are you going to do?"

Jung is one of a new breed of "tribologists" who think that they might have the answer. Tribology—the study of friction, wear, and lubrication—has traditionally been mostly a trial-and-error discipline. But a number of workers in the field are now taking a more systematic, scientific approach—first trying to get a good theoretical understanding of what happens when two surfaces rub against each other in the presence of a lubricant, and then applying that knowledge to produce oils that won't burn into gummy messes in the new high-temperature engines. Their efforts are beginning to pay off.

Current engines, in which the oil reaches a maximum temperature in the range of 350° to 450°F, lose approximately one-third of their energy through the exhaust and another third to the cooling system. About 10 years ago, engineers began to realize that cutting out the cooling system and letting the engine run much hotter would increase fuel efficiency and allow smaller engines to put out more power.



Cummins Engine Company, Inc.

Running hot. *High-temperature engines similar to this Cummins diesel will need a new generation of lubricants to operate.*

"People started designing engines where the top temperature would be 1000°F or more," says Paul Sutor, head of materials science research at Midwest Research Institute in Kansas City, Missouri. "A lot of prototypes were built that couldn't be lubricated," he says, because the engines reached temperatures above the decomposition temperatures of every known oil.

A few years later, the engine designers realized they had left something out of their calculations. A hot engine heats up the air that is drawn into it, making it less dense. Eventually the efficiency gains of higher temperatures are canceled out by the extra work needed to compress the oxygen. Researchers now believe that the most efficient engines will have top oil temperatures of around 700°F, says Marshall Peterson, a tribology consultant in Arnold, Maryland. But this is still too hot for conventional lubricants.

So how does one find a lubricant that works at temperatures high enough to break carbon-carbon bonds, the fundamental molecular bonds in nearly every oil, both natural and synthetic?

Akzo's Jung was presented with exactly this challenge several years ago when he was approached by Ralph Sloan of Cummins Power Systems, a division of Cummins Engine in Columbus, Indiana. Cummins had been under contract to the U.S. Army's Tank Automotive Command to develop an engine that would run without a cooling system. When the company built a high-temperature prototype engine, Sloan recalls, "the lubricants that were commercially available would not work in this engine." So Sloan "looked all over the country to see who had ideas to make it work." He eventually settled on Jung and Akzo Chemicals, the only company he found that was taking a new approach to developing synthetic oils.

Jung's idea was to learn exactly how oils fail at high temperature so that he could design a completely new one that would not. He tested about 20 oils and found that each failed because of deposits in the upper ring area of the piston. The deposits built up, increasing friction to the point where the engine ground to a halt. Chemical analyses of the deposits showed them to be about half carbon deposits, probably from the oxidation of the base oil, and half metal ash from the breakdown of the additives in the oil.

The way to avoid the metal ash turned out to be straightforward, Jung says: replace the existing additives with ashless additives. The harder problem was to find a base stock that would not leave a carbon residue when the engine's temperature hit 700°F.

Jung says he came up with a completely new approach to making a lubricant. Since the engine's temperature was going to be hot enough to break the carbon-carbon bonds in any oil, he decided to put less emphasis on finding a base stock that could take the high temperatures and instead concentrate on finding one that would leave no residues when it decomposed. "You draw molecules on the blackboard," he says, "and theorize about where they will unzip." You then choose a compound whose decomposition leaves smaller molecules because the smaller molecules generally burn off without leaving a residue while larger ones do not burn as well.

This line of reasoning, for instance, allowed Jung to dismiss a whole line of lubricants, the polyol esters, that other researchers thought were good candidates for high-temperature oils. "Knowing the decomposition behavior of polyol esters would immediately eliminate them from your thinking for an oil that will run at 700°F," he says, because they break down into large

pieces that will leave a residue.

Having dismissed polyols, Jung turned to a new base stock whose composition is proprietary information. Although this material does decompose at 700°F, it leaves little residue. Further, although the oil burns, it burns so slowly that oil loss is not a problem, says John Fairbanks of the Department of Energy, who oversees the joint Akzo/Cummins program. Only the thin film of oil along the top ring of the piston at the top of its stroke burns, so the oil losses are not much more than the losses of a conventional oil in a conventional engine.

Along with the base stock, Jung also developed a package of additives based on theoretical considerations. For instance, he says, inorganic chemistry can be used to predict which products are going to attach themselves most firmly to the metal engine parts and thus serve as useful antiwear additives.

Cummins has already tested the synthetic lubricant that Jung developed, and so far it looks like it will not only be a good high-temperature oil but that at lower temperatures it will be far superior to conventional oils, Fairbanks says. In one test, Cummins ran the oil for 300 hours at a top temperature of 850°F, and it had virtually no ash deposit and relatively little oil loss, Fairbanks says. Jung adds that it could be available commercially within a few years and that it will be priced about the same as current synthetic automobile oils, such as Mobil-1.

As a bonus, the new lubricant should help reduce automotive pollution, Fairbanks says. "In conventional engines, 30% to 60% of the particulate emissions come from lubricants," he says. But the Akzo lubricant "should volatize directly into a gas and not form particulates, which will play a major role in reducing emissions."

At the Midwest Research Institute, Sutor also decided that hotter engines would demand a new approach to designing lubricants. "We got tired of trying what you can get off the shelf," Sutor says. So 2 years ago he went "back to first principles" and designed a lubricant "from a clean sheet of paper."

Like Jung, Sutor decided additives were to blame for much of the deposit formation and designed a new set of additives. Unlike Jung, he decided to try to make his base stock more resistant to oxidation. For instance, since longer chain lengths make the molecule more prone to oxidation, he chose a base stock with shorter chain lengths.

Then he went to chemistry to see if he could protect the sites on the base stock molecules that were particularly prone to oxidation. The oxidative attack comes at a particular spot on the chain, he discovered,

Getting a Grip on Rubbing Bodies

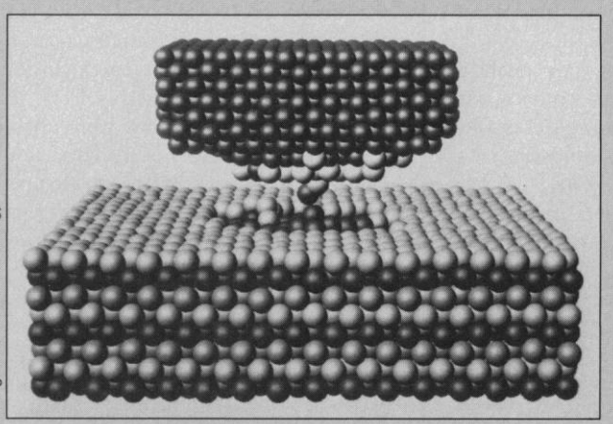
For most of its history, the "science of rubbing bodies" has been an empirical profession—more engineering than predictive science. "There is no unified theory of tribology," says Irwin Singer, a tribologist at the Naval Research Laboratory. And although tribologists believe they understand friction, wear, and lubrication qualitatively, they cannot usually make numerical predictions except by relying on models derived from experimental data.

In the past few years, several theorists have set out to remedy this situation. Their goal is to understand enough about what happens at a molecular level when two surfaces move against each other to be able to suggest new directions and new approaches on the experimental side of tribology. And, although the models they are developing cannot yet handle the complex interactions between surfaces and lubricants, the researchers believe they are laying the groundwork for true science.

For example, Uzi Landman and David Luedtke, two physicists at Georgia Tech, have used molecular modeling on a Cray supercomputer to predict what will happen when the tip of a thin nickel needle is pushed down onto a flat gold surface and then lifted up again. In their model, the needle tip contained 2,000 nickel atoms, while the surface consisted of 8,000 gold atoms. The goal was to calculate the individual trajectories of all 10,000 atoms, which Landman and Luedtke did in two steps.

They first used basic quantum mechanics to determine the electrostatic potential in which each atom moves. "All of the questions of adhesion, cohesion, making of bonds, breaking of bonds—these are really quantum mechanics questions," Landman says. Once the researchers knew the potential, they could calculate the motion of each atom by a straightforward application of Newtonian physics. Straightforward, but definitely not simple. With 10,000 atoms involved, the supercomputer takes up to 150 hours to calculate a motion that in real time takes only a billionth of a second.

The computer simulation shows a quite peculiar action. As the nickel tip approaches the gold surface, the attractive force on the tip increases slowly. Then suddenly, when the tip is about 4 angstroms from the surface, the top layer of gold atoms on the surface breaks loose and bulges out to touch the tip. The gold atoms in the top layer of the surface are more strongly attracted to the nickel atoms in the tip than to their fellow gold atoms, Landman explains. If the tip is now retracted, it pulls a thin neck of gold atoms along with it. After this neck breaks, there is a one-atom-thick coating of gold atoms on the nickel tip and the gold surface is left with one very thin column of atoms pointing up.



Georgia Institute of Technology

Atomic attractions. *As the nickel tip pulls away from the gold surface, it takes a layer of gold atoms (lighter spheres) with it.*

Nancy Burnham and Richard Colton at the Naval Research Laboratory subsequently used an atomic force microscope to check these calculations by observing the interaction between a nickle needle and a gold surface directly. And, Landman says, the behavior they measured was exactly as predicted by the supercomputer.

Such simple theoretical models may be useful in understanding such things as how fractures form, Landman says, but the greater value will appear once researchers model much more complicated systems. "The stage is set for a full interaction between theory and experiment," Landman says. Eventually, he hopes that a theoretical understanding of the molecular forces between two surfaces or between a surface and a lubricant will give scientists a better understanding of what is going on at the macroscopic level. "To make progress in the molecular engineering of lubricants," he says, "you need to know the molecular details of the process." ■ **R.P.**

and he found that blocking that position by adding a side branch would increase the oxidative stability. Unfortunately, this had the effect of making the oil very sluggish at low temperatures. To counteract this, he put the branch a little further down the chain, which improved the viscosity at low temperatures but did not hurt the oxidative stability. "It gets down to the fundamental mechanisms of oxidation," Sutor says.

Researchers are also trying to understand the fundamental properties of solid lubricants with an eye toward improving their performance too. Solid lubricants, such as graphite or molybdenum disulfide (MoS_2), do not reduce friction as well as oils, nor do they perform some of the other jobs of liquid lubricants, such as distributing heat, carrying additives, or collecting dirt for filtration. They are the lubricant of choice, however, in extreme conditions where liquids will not work, such as in very high temperatures or the near vacuum of outer space.

To predict the lubricating ability of a solid, says tribologist Irwin Singer of the Naval Research Laboratory in Washington, D.C., one must understand the interactions between two surfaces and a lubricant as they rub against each other. The motion, heat, and pressure generated in the contact zone cause chemical reactions between the lubricant, the surfaces, and the oxygen in the atmosphere, creating a variety of chemical compounds. These compounds may help or hurt the lubricating action, depending on their structure, so it's important to know what compounds are formed.

Singer and his colleagues have analyzed the solid lubricant MoS_2 in contact with steel and ceramic surfaces. Simple chemistry is enough to predict which compounds will be formed in the contact zone, he says. There are only a finite number of possibilities, and the ones that appear are the ones that are most stable; determining the most stable candidates is a matter of finding the ones with the highest free energy of formation, Singer says. He has checked his predictions by doing experiments with the various materials and then using an electron microscope to determine which compounds were formed in the contact area.

"A good metallurgist could have done this 30 years ago if he had had all the thermodynamic data," Singer says, "but no one has ever done these experiments." Until recently, most tribologists were content to do empirical work without looking at the molecular level to make testable predictions. "What's exciting about it is, it now gives some guidance on how to design lubricants without having to guess," he says.

■ ROBERT POOL

Gene-Transfer Method Fails Test

If science is self-cleansing, then a concerted effort by a number of biologists seems to have mopped up any hope of a new, easy method for putting foreign genes into mice. When Corrado Spadafora reported last June that genes could be transferred by fertilizing mouse eggs with sperm that had been mixed with DNA, researchers around the world began to try to repeat the potentially revolutionary technique. Now, eight of those teams have reported in *Cell* that they cannot, leaving Spadafora, in the same issue, still standing by the work.

The method reported by Spadafora and his colleagues at the University of Rome in the 2 June issue of *Cell* seemed far simpler than the egg injection procedure normally used for making transgenic mice, as mice bearing foreign genes are called. In fact, it seemed a bit too good to be true. And that is what the letter from transgenic mouse pioneer Ralph Brinster of the University of Pennsylvania now says.

In the 20 October issue of *Cell*, Brinster and colleagues report negative results from their laboratory and summarize similar results sent to them by seven other groups. "We believe it is much more difficult to obtain transgenic animals by the incubation of sperm with DNA than reported," the letter states.

"Usually, negative data do not show up anywhere, but in this case at least you have it documented," says Erwin Wagner of the Institute of Molecular Pathology (IMP) in Vienna, whose findings are included in the letter. Although IMP director Max Birnstiel wrote a supportive commentary that accompanied Spadafora's original paper, Wagner says his laboratory's efforts have shown not a glimmer of success. All told, the eight groups analyzed more than 1300 mice generated with the Spadafora technique and found none to carry foreign DNA.

News of difficulty in replicating Spadafora's experiment has been circulating in the transgenic mouse community since mid-summer (see *Science*, 11 August, p. 590). Wagner, who was organizing a mouse molecular genetics meeting to be held in Heidelberg at the end of August, invited Spadafora and his coauthor, Marialuisa Lavitrano, to chair a forum on the technique. They declined—a disappointment, Wagner says, since he had been hoping they could directly address questions about the technique.

Brinster's collaborator, Richard Palmiter of the University of Washington, chaired the session instead and read the letter he and Brinster were preparing to send to *Cell*. When other groups reported negative findings as well, Palmiter invited them to fax their results to Brinster for inclusion in the letter. The data from other groups strengthen the letter, he says. "The point is that lots of different people, doing [the technique] their own way, were unable to reproduce it."

Neither the authors of the letter nor the participants in the Heidelberg forum have declared Spadafora's work erroneous. But it is not repeatable from the information given in the paper, says Brinster, whose group even used reagents borrowed from Spadafora. It is up to Spadafora now, they say, to repeat the technique and teach others how.

That is what Spadafora pledges to do. Although he did not respond to repeated phone calls from *Science*, the 20 October *Cell* also carries a letter in which Spadafora and his colleagues promise to scrutinize their procedure and share any insights about critical steps. They say they have found no reason yet to doubt the experiments, and they rule out a possible mix-up in which traditionally produced transgenic mice might have been confused with those made by the sperm technique. They report that they have begun efforts to replicate the experiments, both in Spadafora's laboratory and elsewhere, and they are further examining the process by which sperm take up DNA. "Although, still in progress, all this work is consistent with previous results that sperm cells may act as vectors for foreign DNA," their letter says.

At a conference at Cold Spring Harbor's Banbury Center last week, Spadafora reportedly told participants that he suspects that the treatment of the sperm may be critical and that reported differences in the fertility of the sperm after treatment suggest that other labs may be performing that part of the procedure incorrectly. "He is very sincere and concerned," said a participant in the Banbury Center conference who requested anonymity. "He is systematically going through all the experiments again, trying all the variables. You can tell he's a bit nervous." ■ MARCIA BARINAGA