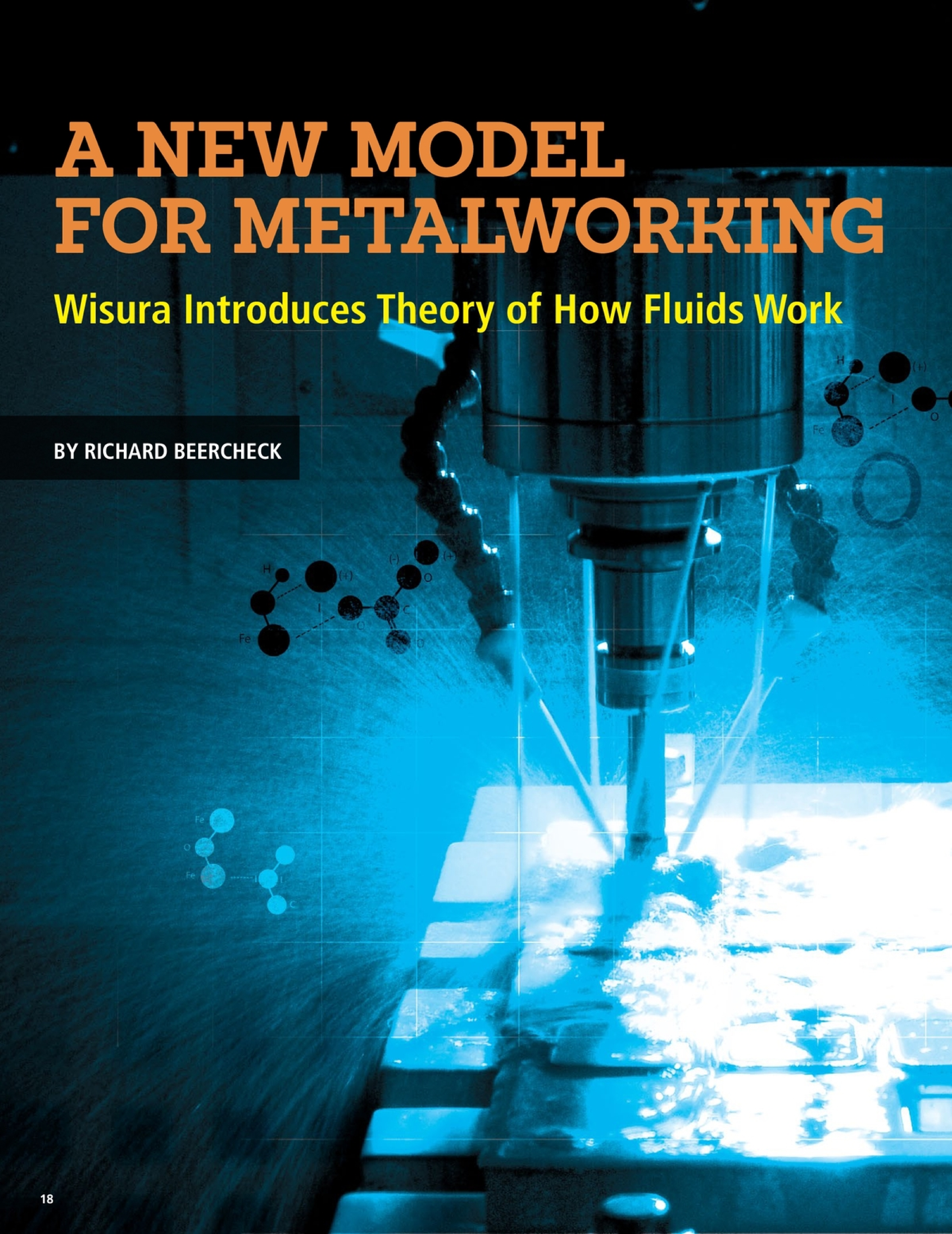
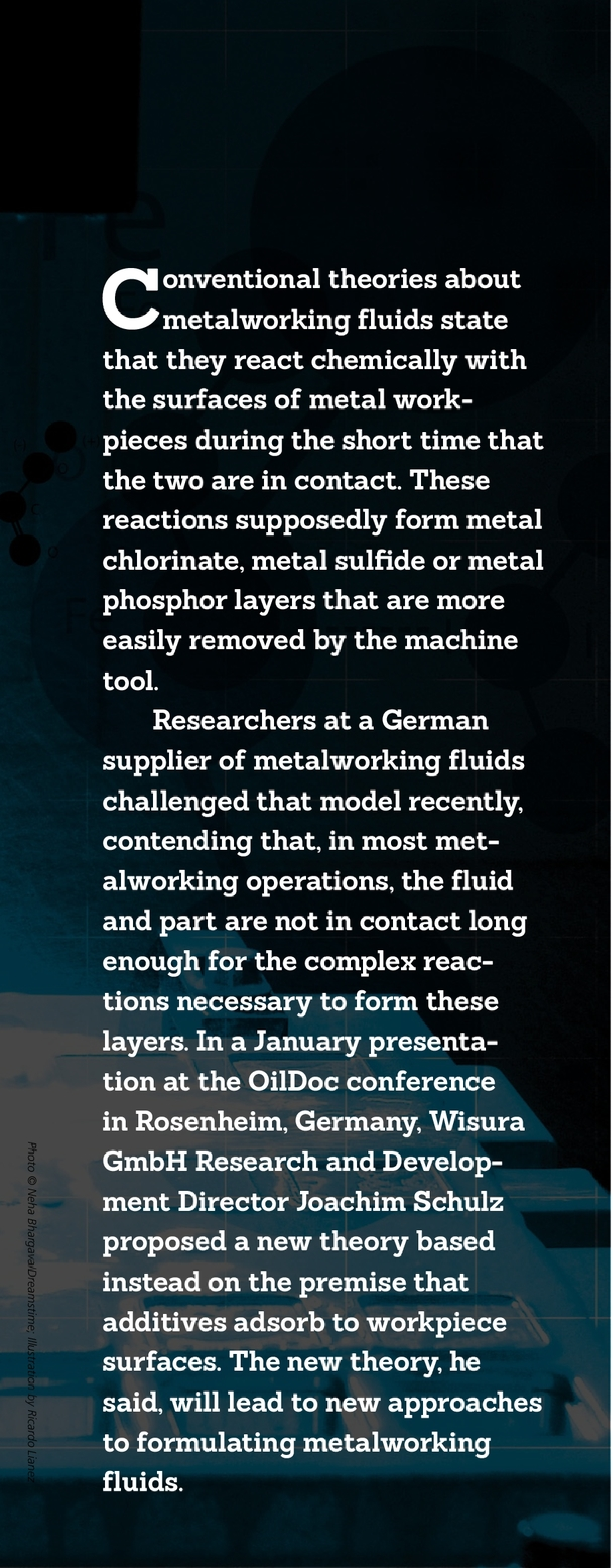
A NEW MODEL FOR METALWORKING

Wisura Introduces Theory of How Fluids Work

BY RICHARD BEERCHECK





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Conventional theories about metalworking fluids state that they react chemically with the surfaces of metal workpieces during the short time that the two are in contact. These reactions supposedly form metal chlorinate, metal sulfide or metal phosphor layers that are more easily removed by the machine tool.

Researchers at a German supplier of metalworking fluids challenged that model recently, contending that, in most metalworking operations, the fluid and part are not in contact long enough for the complex reactions necessary to form these layers. In a January presentation at the OilDoc conference in Rosenheim, Germany, Wisura GmbH Research and Development Director Joachim Schulz proposed a new theory based instead on the premise that additives adsorb to workpiece surfaces. The new theory, he said, will lead to new approaches to formulating metalworking fluids.

Out with the Old

Schulz agrees with one aspect of conventional theories on metalworking fluids: Additives must be interacting with the workpiece in some way to make it more amenable to the metalworking process. Without fluid, metalworking tools generally wear out faster, the finish on workpiece surfaces ends up rougher and the likelihood of adhesion between tool and workpiece increases.

"[S]ome type of reaction is essential to ensure long tool life and to produce an optimum surface finish," he said.

According to Schulz, research supporting the conventional theories has basic flaws. "One difficulty with commonly held theories about metalworking operations," he said, "is that most published literature describes tests in which the additives have a lot of time, often hours, to react with the metal." In addition, most studies do not differentiate between different kinds of metals. "But there is a big difference, for example, in the way carbon steel and stainless steel react," he noted.

Because they were questioning models of interactions with workpieces, Wisura researchers began by studying the atomic structures of various metals used in metalworking. Using secondary ion mass spectroscopy and secondary neutral particle-mass spectroscopy, they found different types of molecules covering surfaces of different metals. Iron surfaces are typically covered with hydroxyl groups, Schulz said, while carbon steel is covered with a layer of hydroxides and oxides. Oxides either cover the entire area or create island-shaped patches. Stainless steels generally are covered by chrome-oxides and nickel-oxides, with the ratio between the two dependent on the specific alloy. And aluminum is covered by a tenacious oxide layer. Thus, steel, stainless steel and aluminum have quite different surfaces and, therefore, react differently with additives.

"Additives interact with oxides, hydroxides or metal ions," said Schulz. Generally, additives are classified as ionic (acidic phosphoric acid esters and passive extreme pressure (PEP) additives) or nonionic (chlorinated paraffins and polysulfides). "Tests show that ionic additives react preferentially with metal ions while nonionic additives react with oxide and hydroxide groups," he said.

Wisura studied the

effectiveness of chlorine- and sulfur-containing additives on various metalworking processes. “Chlorinated oils work in every kind of forming process and with all kinds of materials, especially stainless steel,” he said. “In addition, chlorinated oils work well in high-speed processes like tube or bar drawing. Chlorine-free oils, however, typically do not work on stainless steel, even if the oil and metal are in contact for a long period of time.”

Thus, chlorinated paraffins and sulfur-containing compounds work well on stainless steel, but not PEP additives or acidic phosphoric esters. On the other hand, PEP additives combined with sulfur-containing compounds perform well on carbon steel, as do chlorinated paraffins.

Keeping Time

Schulz talked about the different ways in which chemicals can interact and noted that interaction does not necessarily mean a chemical reaction in which one or more reactants are transformed into new molecules. These reactions require a relatively long time – longer than interactions such as adsorption, where materials with free radicals or ionic charges bond or stick to another.

In light of this fact, Schulz posed the question: “How much time does

Researchers at Wisura concluded that metalworking fluid additives are not in contact with workpieces long enough for complex chemical reactions.

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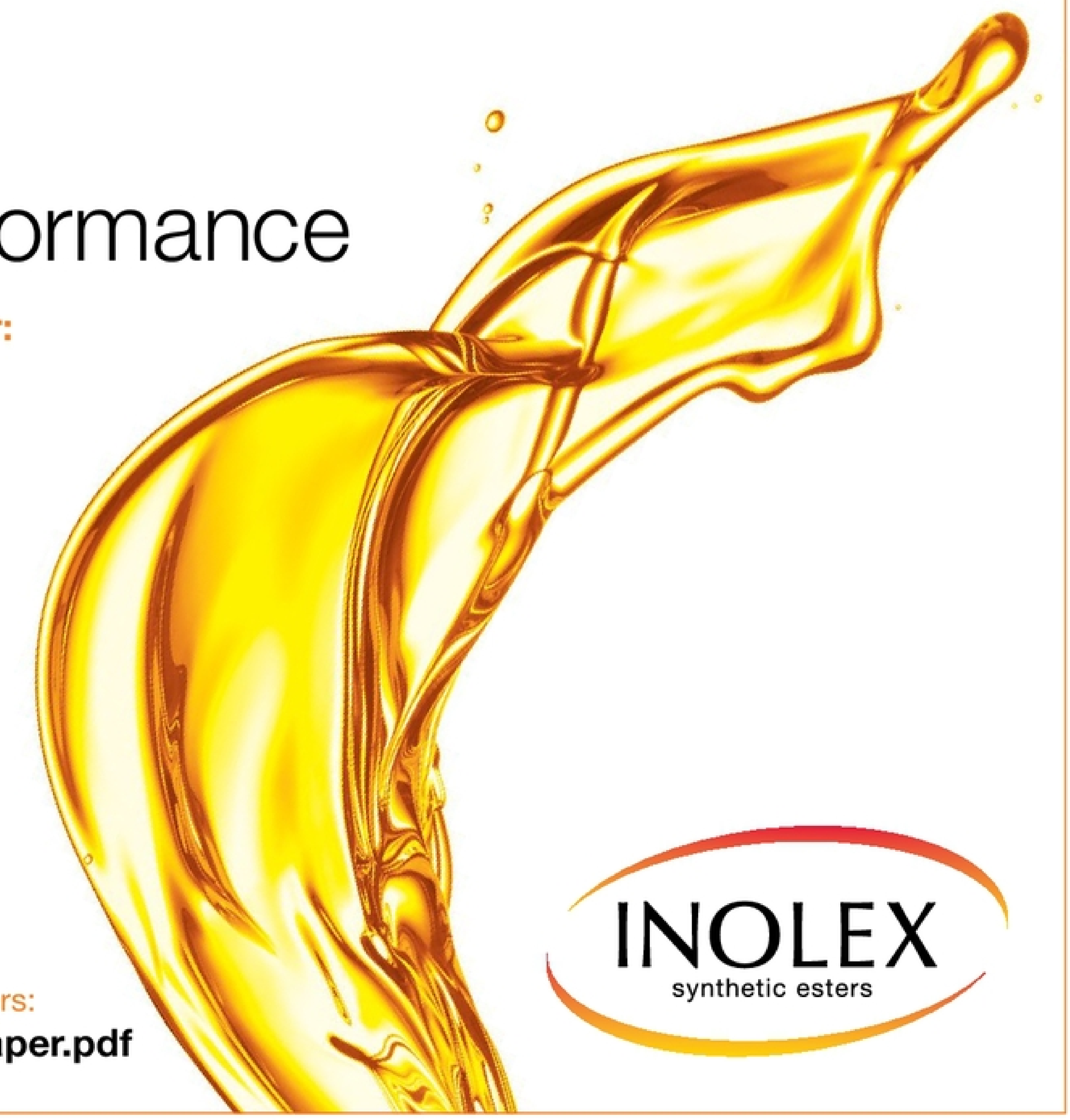
an additive molecule have to interact with the metal surface?" Average machining time depends on the process. For instance, broaching machines work at speeds from six to 30 meters per minute, turning machines at 100 m/min., and grinding machines at circumferential speeds of 100 m/second or more. Wire and tube drawing processes operate at over 50 m/min. Therefore, an average machining time of 60 m/min. means that a 1-millimeter diameter tool contacts a specific area on a part for only a millisecond.

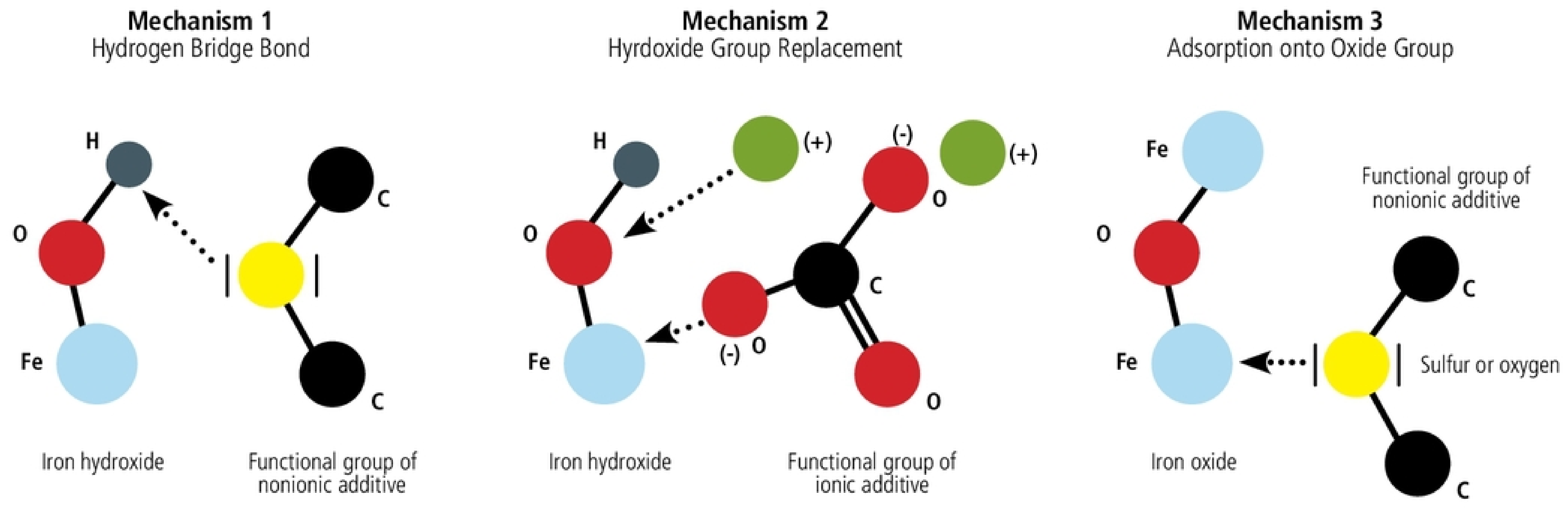
Since that is too little time for full-blown chemical reactions, conventional theories describing the interactions of metalworking fluids must be invalid, and a new one is needed, Schulz said. "The current model is based predominantly on the formation of reaction layers on the metal surface," and surfaces of different metals are assumed to be chemically homogeneous, consisting primarily of oxide layers. In contrast, the new model "minimizes the effects of reactions between additives and metal surfaces and relies mainly on the adsorption effects of additives. This model looks at the chemical nature of metal surfaces in a very different way."

In the new model, additives adsorb to metal surfaces in three possible ways, two for nonionic additives and one for ionic additives. The first mechanism is for the sulfur or oxygen atom of a nonionic additive to bond with a hydroxide group on the metal surface, forming a so-called hydrogen bridge. Under the second, an ionic additive replaces the hydroxide group on the surface. The third mechanism has a nonionic additive adsorbing onto to the metal atoms of an oxide group.

The first and second mechanisms act on the same molecule group and, therefore, compete with each other for sites. "If the metal surface contains both hydroxide and oxide groups, reactions vary between



Additives Interacting with Metal Surfaces



Source: Wisura

Mechanism 1 and 3 or Mechanism 2 and 3. In either case, a synergistic effect should be observed," Schulz said.

These findings show that "classical theories of chemical reaction have only limited application to metalworking processes," Schulz concluded. "The dominant interaction for metalworking fluids is adsorption of the additives to the metal surface. Therefore, cleavage and recombination of molecules are not critical for metalworking operations."

Wisura's research shows that long-chain chlorine- or sulfur-containing paraffins do not react with the metal at the surface temperatures produced and in the time interval common for metalworking operations. "Rather," said Schulz, "the reaction depends on the molecular structure of the metal surface, the type of additive and whether the additive finds an attachment point."

Schulz explained that other research has shown that surface-active additives greatly reduce the energy required for the forming process. This is further evidence that adsorption is the dominant interaction. "Specifically," he said, "surface-active additives increase the flow rates of metals and reduce their fatigue strength." In cutting operations, the additives were shown to stabilize the micro-cracks in metallic materials, preventing them from rewelding, thereby producing smaller chips.

All metalworking processes, including forming, generate fresh metal surfaces, Schulz continued. If these surfaces are not covered immediately by additives, the tool and part can weld together. This effect has been observed most often with stainless steel, aluminum and titanium – materials covered by pure oxide layers – and less frequently with carbon steel or yellow metals. Adhesion occurs because the freshly machined metal is in a highly reactive state and readily forms new chemical bonds. Adhesion can be avoided only if additives quickly adsorb onto the new surface.

Testing the Theory

To test the validity of their new theory, Wisura researchers formulated fluids consisting of triglycerides, fatty acid esters and complex esters in a mixture with 60 percent naphthenic base oil. "Ester-based additives were used because they do not react chemically with other additives or metal surfaces and should work according to both the old and new theories," said Schulz.

The results showed low adsorption rates on stainless steel except for the complex esters. "A possible explanation for this finding is that the electron density and the higher viscosity of the molecules aid adsorption," Schulz explained. Saturated fatty acid esters showed the lowest adsorption because their molecules have fewer binding sites.

On carbon steel, complex esters showed better adsorption because their molecules have more binding sites. Schulz added that "the influence of viscosity cannot be totally excluded although higher viscosity fluids do not always show higher adsorption."

To provide more insight into the impact of esters, they were combined with other additives: a polysulfide, which prefers to bond with oxide groups and to a lesser degree create hydrogen bridge bonds, and overbased sulfonates, which prefer to form ionic bonds.

In theory, the polysulfide should bind preferentially with oxide groups on metal surfaces, thereby inhibiting the adsorption of esters. "Surprisingly," Schulz said, "adsorption values showed the opposite effect, rising with the addition of only 2 percent polysulfide. This means that esters and polysulfides do not compete for the same surface areas, but are complementary in their effects." It also indicates that esters work mainly by creating hydrogen bridge bonds and not by adsorption to the oxide groups.

Schulz said that "higher values on stainless steel are due to the adsorptive effect of the polysulfide because the additive cannot react chemically with the high-grade steel surface."

To corroborate the new theory, mixtures that more closely match commercially available coolants were examined. "The highest adsorption values were produced by triglycerides on carbon steel. The results show that the performance of esters depends on how their oxygen atoms bond with hydrogen atoms of the hydroxides," Schulz said. The same effect was observed on stainless steel.

In the test matrix, the active polysulfide was replaced by a different active polysulfide and in a third trial by an inactive polysulfide. Researchers kept sulfur levels steady in all three cases. The results show that changing the polysulfide had no significant influence on the results. This means that the rate of adsorption depends not on the activity of the polysulfide, but only on the sulfur content itself.

Moving Forward

Schulz concluded by saying, "The results of these tests show that the theory of homogeneous metal surfaces is no longer valid. Recognizing the presence of hydroxides and oxides on the surface leads to good predictions about the behavior of additives or their mixtures. Synergistic and antagonistic effects can be explained by the different affinity of additives to certain surface structures."

Generally, oxide surfaces on stainless steel, aluminum, and titanium are unable to react with ionic additives; rather, they interact only with nonionic additives. The bond between oxygen and iron, chromium or nickel is very stable and cannot be severed by metalworking additives. They can only adsorb onto the surface.

"A surface more or less covered with hydroxides can react with both nonionic and ionic additives," Schulz said. "Reactions between hydroxides and ionic additives replace the hydroxyl-group with the attacking ion. Reactions with nonionic additives create hydrogen bridge bonds."

Finally, Schulz said, "More work is required to describe the activity of other additives such as antiwear compounds. It is to be hoped this investigation can be helped along by transferring the knowledge compiled here about how different additives interact with various surfaces."