



## Acidic all-rounder

There's hardly any limit to the use of formic acid: Beekeepers and farmers appreciate it just as much as airport operators do and mobile phone manufacturers soon will. Keeping high-quality stocks of this acid close to its customers and actively promoting innovations, these are the strengths of BASF - the most important global manufacturer of formic acid that is also the world's leading chemical company. In the summer of 2005, a new production facility for this acid was started up at BASF's new integrated Verbund site at Nanjing/China. Here and at the BASF plant at Ludwigshafen, Germany, the company can now produce a total of up to 230,000 metric tons of formic acid.

Everybody has experienced its stinging effects - in contact with nettles, jellyfish or wood ants (the latter produce more of it each year than all factories taken together, by the way). Ground beetles use it for attack, some caterpillars for defense. But humans, too, have appreciated formic acid for hundreds of years. For example, this acid helps to keep certain foodstuffs fresh and free from salmonellae, and to remove paint and rust from metallic surfaces and scale from kettles and boilers. Breweries and wineries use it for disinfecting barrels, kegs and casks; in the pharmaceutical and crop protectant industries it serves as a pH regulator, and in the cleaning industry it is appreciated as a dirt remover and disinfectant. In all of these applications, the acid offers as welcome side-effect: It is biodegradable.



**Strong performance: Ants produce more formic acid each year than all factories taken together.**



**John Ray, the English naturalist, was the first person to win formic acid in 1671. He heated ant bodies in a flask and collected the distillate.**

Researchers started a long time ago to explore the acidic secret. John Ray, the English naturalist, was the first person to win formic acid in 1671. He heated ant bodies in a flask and collected the distillate. In the mid-19th century, the French chemist Marcellin Berthollet made experiments with oxalic acid and glycerin, and he succeeded: In his flask, the sought-after, pungent-smelling liquid sloshed around.

Since then, the manufacturing principle has changed almost completely. BASF, who has been looking at formic acid since the early 1920s, now makes it from carbon monoxide. Combined with methanol, it first forms methyl formate. In a second step, this is then split up into methanol and formic acid by means of water. The advantage: The product is very pure and does not contain any by-products.

## Spot-on and just-in-time at the customer's

"Reliability and speed of delivery, in addition to the quality of our products, are the major selling points for our customers," explains Joaquim-Filipe Fünfgeld of BASF's Intermediates division, who is in charge of formic acid marketing, inter alia. In order to serve customers flexibly and fast, BASF in Germany uses the services of Pentachemie, a renowned service provider, along with other sales partners. Operating out of Mainaschaff, Hesse, Pentachemie buys formic acid in batches of 20 metric tons from BASF, re-fills it in containers ranging from 60 kilograms to 5 metric tons, as needed by the customer, and then delivers the product. "90 percent of our customers get their goods within one day," Joachim Zimmerer, the general manager of Pentachemie, underlines. "Just-in-time delivery" is the magic term the customer wants to hear, whether he is a beekeeper, a farmer, or the purchasing manager of a pharmaceutical company. Pentachemie serves hundreds of customers in exactly this way.

BASF has a fast track to customers not only in Germany. A global network of storage tanks ensures that the acid is always just where it is needed. There's one tank in Savannah, Georgia, USA; another one in Shanghai, China, and others in Turku, Finland, and Poliport, Turkey. And this year in the summer, a new production facility for formic acid was started up at BASF's new integrated Verbund site at Nanjing, China.

"Our new plant makes us one of the major formic-acid producers in Asia," Fünfgeld says. "We intend to build on this advantage, especially since the demand keeps rising." Up to now, the acid produced in Ludwigshafen was shipped to Asia: From the intermediate stores at Shanghai it was then distributed to end-user customers, for example in the leather industry. Here the acid is used in degreasing and removing hair remnants from hides; it is also used as an additive in dyeing. In South America, Turkey and the south European countries, too, formic acid is mostly sold to the leather industry. For example, Turkey alone has more than 250 tanneries. More than 90 percent of the acid sold in this country is used in the manufacture of leather.

The acid also sells well for rubber production in the plantations of South-East Asia. Latex flows as a milky solution from cuts made in the bark of the rubber tree (*hevea brasiliensis*). Once formic acid is added, this solution coagulates to form rubber-like caoutchouc. It is this step that gives the marketable product, which is processed into mattresses, for example, but also into tires for trucks and cars.

## The preservative par excellence

While in Asia, South America, Turkey and southern European countries, most of the acid is used in leather manufacturing, central and northern Europe sees most of it going to the farming and animal feed industries. In 2003, more than 20 percent of the entire sales volume was used to preserve fresh grass as cattle feed.

Silage, as fermented and therefore preserved fresh grass is called in the trade, was developed by the Finnish scientist and Nobel laureate Artturi Ilmari Virtanen. Forage crops like grass, corn, clover, alfalfa, horse beans, oat and beet leaves are cut and fermented in silos, or covered with air-tight film and stored in the field. Processing grass into silage is particularly popular in the Nordic countries,



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because the humid climate causes grass to spoil fast if it is left unprocessed. Adding formic acid promotes the growth of valuable lactobacilli and prevents the formation of butyric acid, which would spoil the feed. Once it has done its job, formic acid breaks down into carbon dioxide and water - which means it is highly biodegradable.

### Versatile formates

But formic acid can do even more. Just like formic acid as such, diformates - for instance potassium diformate - have antibacterial effects. In animal nutrition, they may even replace the in-feed antibiotics soon to be banned in the EU. Diformates are natural growth promoters for pigs, they prevent intestinal diseases and differ from antibiotics and other drugs in that they are broken down completely by the animals - experts would say, they are "metabolized". BASF recognized these advantages at an early stage.

On the other hand, varroa mites, a bee pest, find the acid hard to digest. Which is why beekeepers bank on formic acid. In many cases, just a sponge soaked in the acid and placed near the bee hive is enough to keep away the deadly invaders. Action is certainly required, for in 2003 alone, one-third of Germany's 800,000 colonies of bees was devastated by the mites.



**Beekeepers use formic acid to fight varroa mites, a bee pest.**



**Runway de-icing with special formic acid salts: Ice and snow are melted highly effective, ensuring better ground grip of the aircraft wheels. In sharp contrast to ordinary de-icing salt there are practically no corrosive effects. And: The acid is biodegradable**

Formic acid is a boon for airport operators, too: Iced-over taxiways are every pilot's nightmare. De-icing agents containing formate are a suitable remedy and highly effective in melting ice and snow. Formates differ from glycols, for instance, in that their effect lasts longer, ensuring better ground grip of the aircraft wheels during take-off and landing. And an important benefit for delicate landing gear is the fact that formates have practically no corrosive effects - in sharp contrast to ordinary de-icing salt. In this field, too, customers appreciate that the acid is biodegradable.

Since their density is relatively high, formates are also important ingredients of drilling fluids, for example when it comes to cooling down the fluid and stabilizing bore holes in natural gas or oil drilling operations.

### BASF supports new applications

"We support our customers in developing new applications for formic acid," Fünfgeld says. "We are happy to help with promising projects." Xavier Sava, whose job it is to prospect for new applications on behalf of BASF, outlines the details of one such project: "40 percent of the paper produced in China is made from straw. Formic acid might substitute the environmentally damaging sulfite used in this process." The acid is needed to crack the plant cell walls to get at the cellulose contained in them: This is the real raw material for paper making. The first facility operating by this principle is expected to start up production at the end of this year. The benefit of formic acid: It can be recycled and reused, which is impossible with sulfite, and it does not harm the environment.

Protecting the environment is also the idea that sparked the use of formic acid in coal-fired power plants. Depending on its origin, coal contains up to five percent sulfur, which is released as sulfur dioxide in the firing process. This environmental toxin causes acid rain, its presence in the atmosphere is therefore undesirable. A process developed in the US removes this gas from the waste air and uses it to make gypsum, a building material. "In this process, formic acid acts as an acid regulator, raising the yield of captured sulfur dioxide from 83 to 95 percent," Sava explains.

In the near future, formic acid will act as an energy source for mobile phones and other portable applications through the use of micro fuel cells. The formic acid fuel cell technology will offer double the operating time of current batteries, allow for instant recharge, and eliminate the reliance on the electrical plug. Formic acid, the versatile "chemical classic", has now made it into the world of high technology. This testifies yet again to what inventive talent can achieve ...



**Salts based on formic acid (formates) are important ingredients of drilling fluids.**

## Formic acid makes airport runways safe for winter take-offs and landings

Ice and snow on airport runways represent a considerable risk. De-icing salts fail to meet expectations. To be sure, they melt ice, but due to their corrosiveness they also pose a hazard to sensitive, highly-stressed landing gears. In the long-run de-icing salts imperil safe operation of the plane.

So that planes can take off and land safely airports spray de-icing agents containing formic acid salts on runways, so-called formiates. Such de-icing agents not only melt ice and snow very effectively, but also sustain its melting effect longer than other agents. Besides they allow airplanes tires better traction on runway surfaces.

It is also a vital consideration that formiates, unlike de-icing salts, have practically no corrosive effect on sensitive landing gears. Another advantage is that the acid is bio-degradable which is why formiates increasingly have the edge over other de-icing agents, such as acetates, for example.



Formic acid makes airport runways safe for winter take-offs and landings

This year BASF, the world's largest producer of formic acid, inaugurated the operation of a formic acid plant at Nanjing, its new, integrated production site in China. Together with another production facility at BASF's manufacturing complex in Ludwigshafen, Germany, the company can now produce up to 230,000 metric tons of formic acid annually.

The product is one of BASF's "evergreens". The company started looking into formic acid in the early twenties. Today it makes the acid out of carbon monoxide which combined with methanol forms methyl formate. In a second step the latter is split by means of water into methanol and formic acid.

Formic acid has many uses. It helps, for instance, to keep certain feeds fresh and free of salmonellae, removes paints and rust from metallic surfaces and scale from kettles and boilers. In breweries and wineries it disinfects kegs, casks and barrels, applied as an auxiliary in the pharmaceutical and crop protection industry it regulates pH values, in cleaning it acts as dirt remover and disinfectant.

Currently researchers are working on making formic acid a source of energy for mobile phones and other portable electronic products equipped with micro fuel cells. Formic acid will provide a considerably longer battery life than conventional storage media. They will also no longer have to rely on being plugged into an electric outlet.