

Rubber, PVC and... bubblegum?

Waldo Semon has a lot to answer for, finds Claudia Flavell-White

WHAT do bubble gum, PVC and tyres have in common? They all owe their commercial success to the same US-born chemical engineer - Waldo Semon.

Well, PVC and tyres certainly do. While Semon did invent a synthetic chewing gum that was great for blowing bubbles, his employer failed to capitalise on that particular patent. But with 216 national and international patents to choose from, one could be forgiven for missing the potential of one of them; especially if it's as far removed from the core business as chewing gum is from a rubber specialist like BFGoodrich.

The enduring commercial importance of PVC cannot be overstated, while Semon's contribution to developing synthetic rubber played an important role in the Allies' victory in World War II.

PVC had been discovered twice, independently, by the German chemist Eugen Baumann in 1872 and the inventor Friedrich Klatte in 1913, who also patented an associated polymerisation process using sunlight. But the material was brittle and no one had any commercial applications for it.

"People thought of PVC as worthless back

then [in the 1920s]" Semon commented when inducted to the US National Inventors Hall of Fame in 1995. "They'd throw it in the trash."

Today, PVC is the world's second most-produced plastic after polyethylene. Two-out-of-three water pipes are made from PVC, as are three quarters of sanitary sewer pipes, with other applications ranging from electrical insulation tape and window frames to phonographic records and credit cards.

The secret ingredient that turned PVC from undesirable waste into million-use product was a solvent which turned PVC from a hard unworkable waste of space into the flexible, bouncy and chemically-resistant multi-use polymer we know today.

a not-so-sticky start

Like so many discoveries, Semon's PVC breakthrough happened by accident, while trying to develop an adhesive that would bond rubber to metal - already big business for BFGoodrich, which had taken on Semon months earlier in mid 1926.

"I thought if I could start with vinyl chloride, polymerise it and then remove the chlorine by some method or other that I might be able to find the conditions to obtain an adhesive

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(Left) Sheet of synthetic rubber coming off the rolling mill at the plant of Goodrich

(Right) Semon earned his PhD in chemical engineering at the University of Washington in 1924

material," Semon told the American Chemical Society in 1966.

Synthesising vinyl chloride and letting the sunlight on the roof of the laboratory polymerise it was easy enough, but removing the chlorine proved to be more problematic. "Among the things I tried was to solvate the PVC in high-boiling solvent and then treat it with zinc or a strong organic amine. Imagine my surprise when I found that the solvated PVC was flexible, resilient and would bounce! When I later found that the plasticised PVC would resist alkaline, strong acids and most solvents it seemed to me that it would have quite a range of commercial possibility."

PVC was clearly not adhesive, but Semon saw its potential and decided to carry on regardless. Plasticised PVC required a lot of energy to heat up and then had to be cooled in the mould, which made the process both time-consuming and expensive. The solution was to produce the raw PVC in the form of a fine powder and then mix it with plasticiser till it resembled a thick paste. "I found I could then spread this paste on cloth or put it in moulds. When it was heated it assumed the same properties that would have been obtained if I'd mixed it first and then moulded the product, but the processing was much easier," Semon said. Known as plastisol technology, the process is still used today.

curtains and camping trips

Like so often, Semon found that it is one thing to find a new product with obvious and promising commercial application, and another thing entirely to sell it to the management. "It took a long time to really interest anyone in PVC," he said. "BFGoodrich at the time was a rubber company. They thought of nothing but rubber and this was not a rubber product, so I had a very interesting experience selling the idea to the management."

The company marketed PVC for a few niche applications such as shoe heels and PVC-coated wire racks for chemical labs but the market was too limited to fund the continued development of PVC. It was the ability to apply PVC to fabrics – coupled with a senior executive's penchant for camping holidays – that catalysed the real breakthrough.

"My wife had been making curtains for the living room," Semon said in an interview with National Public Radio in the US. "I brought some of the fabric into the laboratory and coated it with PVC, and lo and behold, it looked like silk and it was waterproof. I became so enthusiastic, I forgot about protocol and went directly to the vice president of sales [who, as it happens, had

a great love for the outdoors, and a long-standing experience of getting soaked in his supposedly waterproof tent], and he looked at it and he says, 'Hell, what do you mean, waterproof?' So I grabbed the fabric and put it on top of his incoming mail and took a decanter of water and poured it. Oh, he was really frightened, but it didn't leak... I've often wondered what would have happened to me or to PVC if it had leaked."

Semon received the patent for plasticised PVC in 1933, and PVC-coated umbrellas, raincoats and shower curtains followed, as did vinyl records, garden hoses, and a host of other products.

the synthetic rubber race

Meanwhile, Hitler's rise in Germany fuelled US fears that instability in Europe could cut north America off from the Asian natural rubber suppliers it depended on for everything from car tyres to air planes and footwear. Semon's particular mission was to find a synthetic elastomer which could replace natural rubber in automotive tyres. Even without war in Europe threatening to cut off supply lines, natural rubber was in short supply: by the late 1930s, the US consumed over half the world's supply of natural rubber, and the rise of the automotive industry in particular fuelled continuing strong growth – as did indeed the prospect of war, since practically every vehicle used for warfare uses vast quantities of rubber.

The start of the war in 1939 brought the feared cut in supplies, leaving the US with a stockpile that would last no more than 18 months. If no viable synthetic alternative was found in that time, there was no way the US could have won the war.

World War I had catalysed the development of the first synthetic rubber, polymerised methylisoprene, but methyl rubber was an expensive poor imitation and quickly abandoned. German researchers in the 1920s developed 'Buna' (sodium-polymerised butadiene) and found that when they further added styrene and carbon black, the resulting polymer, known as Buna-S, was strong and durable.

Alas, when Semon visited Germany in 1937 with the aim of getting them to share the technology, he found them somewhat protective of the exact details of the process. Semon says: "However, it was really a great experience for me to ride around Germany on tyres made from Buna-S! I came back more enthused than ever and convinced that if Germany would not give us their method for making synthetic rubber, we could develop a process of our own."



It was common knowledge that Buna-S consisted of butadiene and styrene, so 'all' that Semon and his team needed to do was to find some other system of monomers which would not infringe the German patent. What followed was an experimental marathon during which Semon and his team tested every combination of diene monomers and co-monomers they could think of.

"Of the 14,492 experiments we carried out, there were only around 111 promising enough for further detailed development, and of them were only six that looked good enough to be pilot planted," Semon said.

Commercial availability ultimately made the decision in favour of butadiene and methyl methacrylate, already commonly used to make Lucite windows. Semon found that copolymerising 70% butadiene and 30% MMA resulted in a good, abrasion-resistant synthetic rubber – not the cheapest solution but one that was practically available and that would do the job, he says.

A pilot plant for the so-called Ameripol synthetic rubber tyres started up in 1940, and by 1944 some 50 factories across the US alone produced around twice as much synthetic rubber as the world's production of natural rubber before the war.

the gum that would not be

As for the bubble gum – that, alas, was one of Semon's innovations that never got off the ground, even though Semon was very proud of it. An alternative form of bubble gum was already on the market, and Semon's contribution was a synthetic variant that was notable for the huge bubbles one could blow with it. However, BFGoodrich did not see the commercial potential in the innovation, and shelved the product.

Evidently, convincing a rubber and tyre company to enter the foodstuffs business had been just one stretch too far! **tce**

Next month: Luis Miramontes, co-inventor of the oral contraceptive pill